Hot Zone-center Optical Phonons in Laser Irradiated Molybdenum Disulfide

Zherui Han, 1 Peter Sokalski, 2 Li Shi, 2 and Xiulin Ruan 1, *

1 School of Mechanical Engineering and the Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana 47907-2088, USA
2 Walker Department of Mechanical Engineering, The University of Texas at Austin, Austin, Texas 78712, USA

(Dated: August 3, 2022)

Previous multi-temperature-model (MTM) at the polarization level and measurements have uncovered remarkable nonequilibrium among different phonon polarizations in laser irradiated graphene and metals. Here, we show that such a model does not yield observable polarization-based nonequilibrium in laser-irradiated molybdenum disulfide (MoS 2). In contrast, appreciable nonequilibrium is predicted between zone-center optical phonons and the other modes. The momentum-based nonequilibrium ratio is found to increase with decreasing laser spot size and interaction with a substrate. This finding is relevant to the understanding of the energy relaxation process in two-dimensional optoelectronic devices and Raman measurements of thermal transport.

Thermal relaxation of nonequilibrium charge and energy carriers is essential in operating semiconductor devices and laser processing of metals [1, 2]. The energy cascade in such process is usually described as a hierarchical energy flow from an electrical or optical excitation to hot electrons, which are then coupled to optical phonons and finally decayed into the lattice. The efficiency of optoelectronic devices is increased by the so-called “phonon bottleneck” [3–5] associated with the coupling between the hot electrons and phonons. This effect has been captured in previous two-temperature-model (TTM) and its refined successors [1, 2, 6–8] by assigning lumped temperatures to individual carrier subgroups. Recent studies on thermalization of the lattice reveal that the nonequilibrium between the optical and acoustical phonon polarizations and that among different acoustical phonon polarizations can be even more pronounced than that between electrons and phonons [9, 10]. The nonequilibrium inside the lattice phonon bath can give rise to nonthermal melting in devices [11] and inaccurate interpretation of thermal conductivity measurement based on Raman thermometry [9]. Past works have considered nonequilibrium between phonons with different frequency ranges or at different polarizations in the multi-temperature-model (MTM) [9, 12] and the nonthermal lattice model (NLM) [13] that assign different temperatures to each phonon polarization or divide the phonons into low-frequency and high-frequency groups [14]. A polarization-based nonequilibrium has been considered in past studies of graphene [9, 10, 12] as well as a recent study of thin film molybdenum disulfide (MoS 2) [15].

The polarization-based nonequilibrium is a result of different coupling strengths between the hot electrons and different phonon polarizations, such as the three different acoustic phonon branches in a simple metal [13]. In addition, the out-of-plane polarized flexural (ZA) phonons in monolayer graphene show a peculiar quadratic dispersion and is subject to an additional restrictive electron-phonon scattering selection rule compared to that for the other two linear acoustic dispersions [12]. Meanwhile, the size confinement effects on in-plane phonons in nanosized graphene can modify the coupling strength between different phonon polarizations [14].

In this work, we search for potential phonon nonequilibrium in MoS 2 thin films irradiated by a focused laser beam. The usual separation approach based on phonon energies or branches did not yield apparent nonequilibrium. Instead, we find that the zone-center optical phonons are hot by separation of phonons in both the energy and momentum spaces in our first-principles calculations of electron-phonon and phonon-phonon couplings. The calculated degree of nonequilibrium under the same experimental setup agrees well with a concurrent Raman experiment that reports a moderate nonequilibrium [16]. The zone-center optical phonon temperature exceeds those of the other phonon modes increasingly at a reduced laser spot size and by enhanced cooling of the other modes via interface interaction between the MoS 2 thin layer and a substrate. While a prior study [8] has examined momentum-dependent electron-phonon coupling in multilayer tungsten diselenide (WSe 2) irradiated by ultrafast optical pulses, our results reveal that momentum-dependent electron-phonon and phonon-phonon coupling results in hot nonequilibrium phonons in both the energy and momentum spaces. Compared to recent theoretical predictions of zone-center and zone-boundary hot optical phonons in monolayer MoS 2 [17] and MgB 2 [18] during ultrafast pump-probe measurements, our theoretical calculation reveals zone-center hot optical phonons even in relatively thick MoS 2 flakes under steady-state focused laser heating and explains the finding from a concurrent Raman measurement [16].

As illustrated in Fig. 1, our theoretical model considers the general energy pathway for localized laser heating of semiconductors and metals. Upon laser irradiation, electrons gain energy and subsequently dissipate the energy through electron-phonon interactions (EPI). Some phonon polarizations, usually the optical phonons, receive the majority of the dissipated energy and be-
come overpopulated. The excess heat is then lost to the other phonon modes through phonon-phonon scatterings, including three-phonon and four-phonon processes. For a thin-layered material supported by a substrate, phonon-mediated heat transfer across the interface gives rise to an interfacial thermal conductance ($G_i$). Besides mode-dependent electron-phonon and phonon-phonon couplings in the thin layers, mode-dependent phonon coupling across the interface with the substrate phonons, usually characterized by large interface transmission coefficient for low-frequency acoustic vibrational modes [21], is another mechanism that can give rise to nonequilibrium among different phonon modes in the thin layer.

Our first-principles calculations are performed in the framework of Density Functional Theory (DFT) as implemented in Vienna Ab initio Simulation Package (VASP) [22] and we obtain the phononic structure using Density Functional Perturbation Theory (DFPT) [23]. Interatomic force constants are calculated using finite difference method [24]. Phonon-phonon coupling strength is then calculated using a package developed by some authors of the present work, FourPhonon [25]. We use QUANTUM-ESPRESSO [26] along with a modified EPW package [27] to calculate electron-phonon coupling strength and further the electron scattering rates due to phonons. In this framework, coupling strength for a certain phonon mode ($q$) is computed as $\lambda_q = \frac{1}{N_F\omega_q} \sum_{k,k'} |g_{k,k'}^q|^2 \delta_{\omega_k,\omega_q} \delta_{\omega_{k'} + q, \omega_q} [27]$, where $g_{k,k'}^q$ is the electron-phonon coupling matrix element involving electronic state $|k\rangle, |k' + q\rangle$ and phonon mode $|q\rangle$ with frequency $\omega_q$, $\delta$ is the Dirac delta function and $N_F$ is the density of states. Further details on first-principles calculations are presented in Supplemental Materials [28].

An important question is how we should partition and regroup the energy carriers to represent the aforementioned origins of nonequilibrium phonons. For simplicity, we first consider suspended sample and set $G_i = 0$ to examine the effects of mode-dependent electron-phonon and phonon-phonon coupling. We perform first-principles calculations to find spectral electron-phonon and phonon scatterings. Figure 2 shows our calculated mode-wise electron-phonon scattering and phonon-phonon scatterings that are mapped onto phonon dispersions in bulk MoS$_2$. We observe from Fig. 2(a) that electrons are mainly coupled with zone-center phonons and the coupling strength ($\lambda_q$) for a certain mode specified by its momentum ($q$) shows a strong dependence on the wavevector for each phonon branch. Additionally, some optical phonons with low frequencies and near the zone center still show strong coupling with electrons. This feature implies that grouping phonons only by their energy range or phonon branches may not be sufficient for this particular material. The calculated electron linewidth as a function of the electron energy is also shown in Fig. 2(b). In addition, we also obtain the electron-phonon coupling factor $G_{ep}$ for energy flow from electrons into different phonon groups. As shown by the calculated phonon-phonon scattering rates in Fig. 2(c,d), optical phonons have higher scattering rates that generally increases with increasing phonon frequency. A detailed analysis into different phonon scattering channels in Fig. 2(d) indicates that phonon-phonon scatterings ($\tau_{4ph}^{-1}$) are generally one magnitude lower than three-phonon counterpart ($\tau_{3ph}^{-1}$). Thus, in the present work we only calculate phonon coupling factors $G_{pp}$ based on three-phonon scattering rates. In our work, the coupling factors $G_{ep}$ and $G_{pp}$ are all obtained through first-principles calculations.

In previous works [9, 12], the standard multi-temperature-model (MTM) resolves phonons at the polarization level without differentiating phonons from the same branch at different momentum spaces. Based on our mode-wise scattering rate calculation results for MoS$_2$, we specify five different equivalent temperatures for electrons, zone-center optical phonons, high-frequency non-zone-center optical phonons, low-frequency non-zone-center optical phonons, and acoustic phonons. In this way, the previous MTM is extended to resolve phonons in both energy and momentum spaces. In the following corresponding energy equations that are modified from the previous MTM [9, 12], the subscript $e$ represents electrons and $\{p, i\}$ represents a certain phonon subgroup. $C$ denotes specific heat, $\kappa$ is the thermal conductivity, $T$ is temperature and $G$ is the coupling factor for each subgroup, $Q$ is external energy source. For electrons the energy balance reads

$$C_e \frac{\partial T_e}{\partial t} = \nabla (\kappa_e \nabla T_e) - \sum_i G_{ep,i} (T_e - T_{p,i}) + Q. \quad (1)$$
For each phonon subgroup $i$, we have

$$C_{p,i} \frac{\partial T_{p,i}}{\partial t} = \nabla \cdot (\kappa_{p,i} \nabla T_{p,i}) + G_{e,p,i} (T_e - T_{p,i}) + G_{p,p,i} (T_{lat} - T_{p,i}). \tag{2}$$

In particular, we define a lattice reservoir $T_{lat}$ with which all phonon subgroups should exchange energy: $\sum G_{p,p,i} (T_{lat} - T_{p,i}) = 0$. By doing this, the phonon coupling factors are easily related to the phonon lifetime $\tau_i$ under relaxation time approximations (RTA): $G_{p,p,i} = \frac{C_{p,i}}{\tau_i}$. $Q$ represents the absorbed Gaussian laser power density in an axisymmetric system and it reads $Q(r, z) = \alpha I(r, z)$ with $I(r, z)$ being the laser intensity profile [29]:

$$I(r, z) = \frac{2P(1-R)}{\pi w(z)^2} e^{-\frac{2r^2}{w(z)^2} - \alpha z}. \tag{3}$$

$P$ denotes the laser power, $R$ is the reflectance, $\alpha$ is the absorption coefficients of the sample, and $w(z)$ is the laser beam divergence relation at a certain depth $z$ (these parameters are discussed in Supplemental Materials [28]). Equation 1 and 2 can then be solved numerically in real-space with axisymmetric boundary conditions, and in this work this system of partial differential equations is solved using finite element methods in COMSOL Multiphysics [30].

Figure 3 compares the calculation results from the previous branch-wise MTM and the present momentum-resolved MTM model. The branch-wise MTM assigns two different average phonon temperatures, one for the optical branches and the other for the acoustic branches. While this branch-wise MTM can reveal phonon nonequilibrium in metals and graphene [9, 12–14], it cannot produce any observable nonequilibrium in bulk MoS$_2$, as shown in Fig. 3(a). In comparison, the momentum-resolved MTM model reveals apparently higher temperatures for the zone-center optical phonons than $T_{lat}$. This result suggests that in the zone-center optical phonons in bulk MoS$_2$ are coupled preferentially to electrons and are not effectively cooled down by the lattice. Based on this result, phonon nonequilibrium in laser irradiated MoS$_2$ mainly occurs in the momentum space between the zone center modes and other modes, instead of between phonons of different polarizations. Essentially, the energy flow bottleneck is mainly in the momentum space instead of across the different energy ranges or polarizations.

We define a nonequilibrium ratio as $\xi = \Delta T_h/\Delta T_{lat}$ between the temperature rise of the hottest group ($\Delta T_h$) and that of the lattice ($\Delta T_{lat}$). In the case of bulk MoS$_2$, $\Delta T_h$ is the temperature rise ($\Delta T_{op}$) of the zone-center optical phonons. In Fig. 4(a) that has accounted for the effect of the laser-induced temperature rise, this ratio is obtained as the slope of the calculated $\Delta T_{op}$ versus $\Delta T_{lat}$ at different laser power and each laser spot size.
for suspended sample. Though the change of nonequilibrium with respect to laser power is marginal in this system (indicated by the almost linear relation in Fig. 4(a)), the numerical solutions do show a decrease of nonequilibrium with higher laser power level. This power dependence is in agreement with and explained in the prior study of graphene [10]. Our simulated nonequilibrium ratio under the same experimental condition is 1.21 when \( r = 0.71 \mu m \), in good agreement with Ref. [16]. Compared to the degree of phonon nonequilibrium observed in graphene (\( \xi > 2 \)) [9, 10], this reduced ratio is understandable as bulk MoS\(_2\) has lower thermal conductivity and generally stronger phonon scatterings than graphene.

Additionally, the ZA mode in graphene couples weakly with other phonon modes and essentially cools down the lattice. When the Gaussian laser beam radius decreases from 1.15 \( \mu m \) to 0.71 \( \mu m \) and approaches the thermalization length of hot zone-center phonons, the zone-center phonons are not able to thermalize with the lattice within the laser spot, resulting in a higher \( \xi \) at a smaller laser spot size.

We further examine the effect of substrate phonon coupling on the nonequilibrium ratio, as the findings will have practical implications for electronic devices made with supported MoS\(_2\) layers [31]. Thus, we choose a model sample with a thickness of 10 nm on SiO\(_2\) substrate in this case. Acoustic phonon modes of SiO\(_2\) lie in the same frequency range as MoS\(_2\) (~5 THz). Since high-group-velocity acoustic phonons usually have the dominant contribution to the interface conductance and considering the fact that the low-frequency optical phonons in bulk MoS\(_2\) are in near equilibrium with the lattice, in our model the interface conductance term is only added to acoustic phonon group, where the energy outflow to the substrate is proportional to the temperature difference between the acoustic group \((p, a)\) and the substrate \((T_{sub})\):

\[
C_{p,a} \frac{\partial T_{p,a}}{\partial t} = \nabla (\kappa_{p,a} \nabla T_{p,a}) + G_{cp,a} (T_e - T_{p,a}) + G_{pp,a} (T_{lat} - T_{p,a}) - G_t (T_{p,a} - T_{sub}),
\]

As shown in Fig. 4(b), an increase in the interface conductance \( G_t \) would decrease the overall lattice temperature rise \( \Delta T_{lat} \) more than \( \Delta T_{op} \) for a given laser power level and laser spot size, because \( \Delta T_{lat} \) is cooled directly by interface heat transport mainly caused by interface coupling of acoustic phonons. Consequently, the nonequilibrium ratio \( \xi \) increases with \( G_t \).

These results show that the conventional phonon branch-wise multi-temperature-model (MTM) does not yield any observable phonon nonequilibrium in laser-irradiated MoS\(_2\). However, when we extend the model to have both energy and momentum dimensions, a moderate nonequilibrium is produced and can explain the experimental data in Ref. [16]. This implies that thermal equilibrium is well established between phonon groups having different energy states, but not between phonons with different momenta even in the same branch. Only the extended MTM that treats the zone-center phonon separately, while not the conventional phonon branch-wise MTM, can predict the phonon nonequilibrium that is observed in concurrent experiments. Based on this finding, whether phonons should be resolved in both energy and momentum space should be based on first-principles calculations of electron-phonon and phonon-phonon interactions. The degree of hot zone-center optical phonons is increased with reduced laser spot size and substrate coupling of acoustic modes. These findings provide detailed insights on phonon nonequilibrium
phenomena in optically or electrically excited functional materials and devices.

X. R., Z. H., and L. S., P. S. were supported by two collaborating grants (No. 2015946 and No. 2015954) of the U.S. National Science Foundation. Simulations were performed at the Rosen Center for Advanced Computing (RCAC) of Purdue University.

* ruan@purdue.edu

[1] P. B. Allen, Theory of thermal relaxation of electrons in metals, Physical Review Letters 59, 1460 (1987).

[2] S. Sadasivam, M. K. Y. Chan, and P. Darancet, Theory of Thermal Relaxation of Electrons in Semiconductors, Phys Rev Lett 119, 136602 (2017), 1709.00451.

[3] J. Urayama, T. B. Norris, J. Singh, and P. Bhattacharya, Observation of phonon bottleneck in quantum dot electronic relaxation, Physical review letters 86, 4930 (2001).

[4] A. J. Nozik, Quantum Dot Solar Cells, Physica E: Low-dimensional Systems and Nanostructures 14, 115 (2002).

[5] J. Yang, X. Wen, H. Xia, R. Sheng, Q. Ma, J. Kim, P. Tapping, T. Harada, T. W. Kee, F. Huang, et al., Acoustic-optical phonon up-conversion and hot-phonon bottleneck in lead-halide perovskites, Nature communications 8, 1 (2017).

[6] T. Qiu and C. Tien, Short-pulse laser heating on metals, International Journal of Heat and Mass Transfer 35, 719 (1992).

[7] A. Majumdar and P. Reddy, Role of electron–phonon coupling in thermal conductance of metal–nonmetal interfaces, Applied Physics Letters 84, 4768 (2004).

[8] L. Waldecker, R. Bertoni, H. Hübener, T. Brumme, T. Vasileiadis, D. Zahn, A. Rubio, and R. Ernstorfer, Momentum-Resolved View of Electron-Phonon Coupling in Multilayer WSe2, Physical Review Letters 119, 036803 (2017), 1703.03496.

[9] A. K. Vallabhaneni, D. Singh, H. Bao, J. Murthy, and X. Ruan, Reliability of Raman measurements of thermal conductivity of single-layer graphene due to selective electron-phonon coupling: A first-principles study, Phys Rev B 93, 125432 (2016).

[10] S. Sullivan, A. Vallabhaneni, I. Kholmanov, X. Ruan, J. Murthy, and L. Shi, Optical Generation and Detection of Local Nonequilibrium Phonons in Suspended Graphene, Nano Lett 17, 2049 (2017), 1701.03011.

[11] Y. Wang and X. Xu, Molecular dynamics studies of ultrafast laser-induced nonthermal melting, Applied Physics A 110, 617 (2013).

[12] Z. Lu, A. Vallabhaneni, B. Cao, and X. Ruan, Phonon branch-resolved electron-phonon coupling and the multitemperature model, Physical Review B 98, 134309 (2018).

[13] L. Waldecker, R. Bertoni, R. Ernstorfer, and J. Vorberger, Electron-Phonon Coupling and Energy Flow in a Simple Metal beyond the Two-Temperature Approximation, Physical Review X 6, 021003 (2016), 1507.03743.

[14] M. An, Q. Song, X. Yu, H. Meng, D. Ma, R. Li, Z. Jin, B. Huang, and N. Yang, Generalized Two-Temperature Model for Coupled Phonons in Nanosized Graphene, Nano Letters 17, 5805 (2017), 1702.05237.
X. Li, L. G. Marshall, X. Ma, N. Klimovich, J. Zhou, L. Shi, and X. Li, Magnons and Phonons Optically Driven out of Local Equilibrium in a Magnetic Insulator, Physical Review Letters 117, 107202 (2016), 1601.01982.

[30] COMSOL, Inc, Comsol multiphysics v. 5.6., www.comsol.com.

[31] W. Zheng, C. J. McClellan, E. Pop, and Y. K. Koh, Nonequilibrium Phonon Thermal Resistance at MoS2/Oxide and Graphene/Oxide Interfaces, ACS Applied Materials & Interfaces 14, 22372 (2022).
Supplemental Material for “Hot Zone-center Optical Phonons in Laser Irradiated Molybdenum Disulfide”

Zherui Han,1 Peter Sokalski,2 Li Shi,2 and Xiulin Ruan1,*

1School of Mechanical Engineering and the Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana 47907-2088, USA
2Walker Department of Mechanical Engineering, The University of Texas at Austin, Austin, Texas 78712, USA

(Dated: August 3, 2022)
CONTENTS

Sec.1. First-principles calculations for electron-phonon and phonon-phonon couplings 2

Sec.2. Temperature dependence of coupling parameters in the extended MTM 3

Sec.3. Finite-element modeling of heat transfer in an axisymmetric system 5

References 6

Section 1. FIRST-PRINCIPLES CALCULATIONS FOR ELECTRON-PHONON AND PHONON-PHONON COUPLINGS

In this section, we cover the computational details in our first-principles calculations to obtain input parameters in the extended MTM.

All calculations are done using Density Functional Theory (DFT) or Density Functional Perturbation Theory (DFPT). For structural optimization, we use $k$-grid of $12 \times 12 \times 3$ with 520 eV plane wave energy cutoff. To describe van der Waals (vdW) interactions in bulk MoS$_2$, we employ a DFT-D3 correction method [1]. For electron-phonon interactions, all calculations are done using the QUANTUM-ESPRESSO package [2] with Perdew-Burke-Ernzerhof exchange-correlation functional [3], norm-conserving pseudopotentials [4], and a kinetic energy cutoff of 50 Ry. The EPW package [5] is employed to perform Wannier function interpolation for the e-ph coupling matrix elements. The related quantities are calculated first on a coarse grid of $8 \times 8 \times 2$ and then Wannier interpolated into a fine grid of $32 \times 32 \times 8$ for electron linewidth, and $16 \times 16 \times 4$ $q$-mesh for phonon self energy. The electronic integration over the Brillouin Zone (BZ) is approximated by the Gaussian smearing of 0.02 eV for the self-consistent calculations.

For phonon-phonon interactions in bulk MoS$_2$, we employ the VASP package [6] and use Perdew-Burke-Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA) for exchange and correlation functionals [3]. The plane wave cutoff is 520 eV. We also construct $4 \times 4 \times 1$ supercells and use $3 \times 3 \times 2$ $k$-mesh to calculate interatomic force constants (IFCs) and consider 0.5 nm cutoff and the second nearest neighboring atoms for the third-order IFCs and fourth-order IFCs, respectively. The BZ is discretized by $12 \times 12 \times 4$ $q$-mesh.

*ruan@purdue.edu
to evaluate three-phonon scattering rates using ShengBTE package [7] and four-phonon scattering rates using the FourPhonon tool [8]. The mode-resolved thermal conductivity is computed using a slightly modified version of the FourPhonon package. The broadening factor for the three-phonon calculations is unity. In this work, the thermal expansion and phonon renormalization effects are not included.

Sec.2. TEMPERATURE DEPENDENCE OF COUPLING PARAMETERS IN THE EXTENDED MTM

In the extended MTM, the input parameters should in principle all be temperature-dependent but their detailed mechanisms of temperature dependence are different. For electron relaxation, the coupling factor is computed as $G_{ep,i} = \frac{C_e}{\tau_{e,i}}$ where $C_e$ is the electron specific heat and $\tau_{e,i}^{-1}$ is the electron scattering rates (or electron linewidth) due to phonon subgroup $i$. Electron specific heat $C_e$ is computed as the derivative of electron energy with respect to the electron temperature $T_e$:

$$C_e(T_e) = \int_{-\infty}^{\infty} \rho(\varepsilon)\varepsilon \frac{\partial f(\varepsilon - \mu, T_e)}{\partial T_e} d\varepsilon,$$

(S.1)

where $\rho$ is the electron density of states, $f$ is the Fermi-Dirac distribution, $\mu$ is the electronic chemical potential and $\varepsilon$ is the electron energy. In principle, $G_{ep,i}$ and $\tau_{e,i}^{-1}$ have complicated temperature dependence on both electron temperature and phonon temperature, as higher electron temperature means more electrons are excited into higher energy states, and higher phonon temperature means greater scattering with electrons. In Ref. [9], this is captured by several third-order polynomials with two independent variables $T_e$, $T_{p,i}$ and a fitting into experimental data at some temperatures. In Ref. [10], the authors proposed a more convenient way such that electron specific heat $C_e$ has a linear dependence on $T_e$ and it makes $G_{ep,i}$ insensitive on $T_e$ altogether. This consideration simplifies the temperature dependence here and in this work we can express $G_{ep,i}(T) = G_{ep,i}(T_{p,i})$. We can then evaluate electron scattering rates for an electron state $k$ due to phonon group $i$ at a phonon group temperature:

$$\frac{1}{\tau_{k,i}(T)} = \sum_{q \in i} |g_{k,q}|^2 \left\{ [(f_{k+q} + n_q) \delta (\varepsilon_{k+q} - \varepsilon_k - \hbar \omega_q)] + [(1 + n_q - f_{k+q}) \delta (\varepsilon_{k+q} - \varepsilon_k + \hbar \omega_q)] \right\},$$

(S.2)
where we perform summation over phonon modes \( q \) in subgroup \( i \), and \( f \) and \( n \) are Fermi-Dirac and Bose-Einstein distributions, respectively. \( \varepsilon \) is the corresponding electronic state energy and \( \omega \) is the phonon frequency.

For phonon relaxation, the coupling factor is computed as \( G_{pp,i} = \frac{C_{p,i}}{\tau_i} \). The mode contribution specific heat \( C_{p,i} \) can be evaluated by

\[
C_{p,i}(T) = \frac{k_B}{\Omega N} \sum_i \left( \frac{h \omega}{k_B T} \right)^2 n_0 (n_0 + 1),
\]

(S.3)

where \( \omega \) is the phonon frequency, \( \Omega \) is the BZ volume, \( N \) is the number of sampling grid, and \( n_0 \) is the occupation number of phonons at equilibrium. The summation is over phonons in group \( i \). In the above equation, temperature dependence is on the temperature of the current group \( T = T_{p,i} \). The phonon relaxation rate \( \tau_i^{-1} \) can be evaluated by the averaged three-phonon scattering rates in that subgroup at the RTA level since we have defined a lattice reservoir. We note that a prior work without lattice reservoir used empirical estimation here [10]. For one phonon mode \( \lambda \), its scattering rate involving two other phonons \( (\lambda', \lambda'') \) and phonon absorption (+) and emission (-) processes can be computed by Fermi’s golden rule:

\[
\frac{1}{\tau_{\lambda}} = \frac{1}{N} \left( \sum_{\lambda' \lambda''} \Gamma_{\lambda' \lambda''}^{(+)} + \sum_{\lambda' \lambda''} \frac{1}{2} \Gamma_{\lambda' \lambda''}^{(-)} \right),
\]

(S.4)

\[
\Gamma_{\lambda' \lambda''}^{(+)} = \frac{\hbar \pi}{4} \left( n_{\lambda'}^0 - n_{\lambda''}^0 \right) \omega_{\lambda'} \omega_{\lambda''} | V_{\lambda' \lambda''}^{(+)} |^2 \delta (\omega_{\lambda'} + \omega_{\lambda''} - \omega_{\lambda''}),
\]

(S.5)

\[
\Gamma_{\lambda' \lambda''}^{(-)} = \frac{\hbar \pi}{4} \left( n_{\lambda'}^0 + n_{\lambda''}^0 + 1 \right) \omega_{\lambda'} \omega_{\lambda''} | V_{\lambda' \lambda''}^{(-)} |^2 \delta (\omega_{\lambda'} - \omega_{\lambda''} - \omega_{\lambda''}),
\]

(S.6)

where \( V_{\lambda' \lambda''}^{(\pm)} \) is the transition probability matrices elements and \( \delta \) is the Dirac function. The temperature dependence of scattering rate \( \tau_i^{-1} \) is then implicitly included in the occupation number of the interacting phonon modes \( n_{\lambda'}^0, n_{\lambda''}^0 \). This calculation then yields that \( \tau_i^{-1}(T) \) should depend on the lattice bath temperature, or \( T = T_{lat} \). Based on these discussions, we can compute temperature-dependent phonon properties and find that \( C_{p,i} \) has weak temperature dependence in the range of 300 K to 800 K (see Fig. S1(a)) and \( \tau_i^{-1} \) is linearly related to lattice temperature (see Fig. S1(b)). In this study, we can neglect \( C_{p,i}(T) \) and write the coupling factor as \( G_{pp,i}(T) = \frac{C_{p,i}}{\tau(\text{lat})} \), which is a function of lattice temperature.
FIG. S1. Temperature-dependent phonon properties of four subgroups in this study: (a) specific heat and (b) phonon scattering rates.

Sec.3.  FINITE-ELEMENT MODELING OF HEAT TRANSFER IN AN AXISYMMETRIC SYSTEM

In accordance with typical micro-Raman experiments, we create an axisymmetric system with sample suspended over a circular hole and two ends supported by Au/SiO$_2$ substrate. In such case, our extended MTM should be solved in 2D real space using finite-element method. We choose the mathematical module in a commercial solver COMSOL Multiphysics [11].

Since we divide the carriers into five representative subgroups, the system of partial differential equations describing the temperature field is of five dimensions with five independent variables $u = [T_1, T_2, T_3, T_4, T_5]^T$ and the derivative operator $\nabla = [\frac{\partial}{\partial r}, \frac{\partial}{\partial z}]$. In COMSOL, this is realized by the Coefficient Form of PDE solver. The reference temperature is set as 300 K and we have applied Dirichlet boundary conditions to this real space heat transfer problem. This includes prescribed temperatures of 300 K for all subgroups at the outer radial boundary, i.e., the system reaches thermal equilibrium at the boundary. In the case of a supporting substrate, we apply an outward flux term to acoustic phonon group.

To compare with Raman experiment, one needs to average the temperature field to get experimentally probed Raman temperatures [12]. For a temperature field $T(r, z)$, if we assume a Gaussian laser beam the weighted Gaussian average temperature $\langle T \rangle$ reads
\[
\langle T \rangle = \frac{\int_0^\infty dz \int_0^\infty rdr T(r,z)Q(r,z)}{\int_0^\infty dz \int_0^\infty rdr Q(r,z)} \tag{S.7}
\]
where in the main text we define \( Q(r,z) = \alpha I(r,z) \) with \( I(r,z) \) being the laser intensity profile. The laser beam divergence relation \( w(z) \) mentioned in the main text is calculated as
\[
w(z) = w(0) \sqrt{1 + (z/\beta)^2}
\]
with \( w(0) \) being the laser spot size in radius and \( \beta = \pi w(0)^2 n \lambda \), where \( n \) is the indexes of refraction and \( \lambda \) is the laser wavelength [13]. In this work, we use the experimentally determined optical parameters to better reflect actual energy inflow to the system. In particular we have absorption coefficients \( \alpha = 4.35 \times 10^5 \text{ cm}^{-1} \), reflectance \( R = 0.67 \), refractive index \( n = 4.77 \), laser wavelength \( \lambda = 532 \text{ nm} \). The power level and laser spot size are reported in Ref. [13]. The simulated temperature profile in such a radial system is shown in Fig. S2 when laser power is \( P = 2.35 \text{ mW} \) and spot size is \( r = 0.71 \mu \text{m} \). The Gaussian averaged temperatures for zone-center phonons and the lattice in this case are 384 K and 397 K, respectively.

![Zone-center phonon and lattice temperature profiles](image)

**FIG. S2.** Simulated temperature profile \( T(r,z) \) (unit: K) for zone-center optical phonons and lattice bath. Sample is suspended and has a thickness of 72 nm.

---

[1] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *The Journal of Chemical Physics* **132**, 154104 (2010).
[2] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. d. Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials, J. Phys. Condens. Matter 21, 395502 (2009), 0906.2569.

[3] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77, 3865 (1996).

[4] N. Troullier and J. L. Martins, Efficient pseudopotentials for plane-wave calculations, Phys. Rev. B 43, 1993 (1991).

[5] S. Poncé, E. Margine, C. Verdi, and F. Giustino, EPW: Electron–phonon coupling, transport and superconducting properties using maximally localized Wannier functions, Comput. Phys. Commun. 209, 116 (2016), 1604.03525.

[6] G. Kresse and J. Hafner, Ab initio molecular dynamics for liquid metals, Phys. Rev. B 47, 558 (1993).

[7] W. Li, J. Carrete, N. A. Katcho, and N. Mingo, ShengBTE: A solver of the Boltzmann transport equation for phonons, Comput. Phys. Commun. 185, 1747 (2014).

[8] Z. Han, X. Yang, W. Li, T. Feng, and X. Ruan, FourPhonon: An extension module to ShengBTE for computing four-phonon scattering rates and thermal conductivity, Comput. Phys. Commun. 270, 108179 (2022).

[9] A. K. Vallabhaneni, D. Singh, H. Bao, J. Murthy, and X. Ruan, Reliability of Raman measurements of thermal conductivity of single-layer graphene due to selective electron-phonon coupling: A first-principles study, Phys Rev B 93, 125432 (2016).

[10] D. Novko, F. Caruso, C. Draxl, and E. Cappelluti, Ultrafast Hot Phonon Dynamics in MgB2 Driven by Anisotropic Electron-Phonon Coupling, Physical Review Letters 124, 077001 (2020), 1904.03062.

[11] COMSOL, Inc, Comsol multiphysics v. 5.6., www.comsol.com.

[12] K. An, K. S. Olsson, A. Weathers, S. Sullivan, X. Chen, X. Li, L. G. Marshall, X. Ma, N. Klimovich, J. Zhou, L. Shi, and X. Li, Magnons and Phonons Optically Driven out of Local Equilibrium in a Magnetic Insulator, Physical Review Letters 117, 107202 (2016), 1601.01982.
[13] P. Sokalski, Z. Han, G. C. Fleming, B. Smith, S. E. Sullivan, R. Huang, X. Ruan, and L. Shi,
Effects of hot phonons and thermal stress in micro-raman spectra of molybdenum disulphide,
arXiv preprint 10.48550/arxiv.2206.15473 (2022).