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Carlos da Silva, Cristina H. Amon

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Predicting Phonon Thermal Transport in Strained Two-dimensional Materials: Graphene, Boron Nitride, and Molybdenum Disulfide

Carlos da Silva, Cristina H. Amon
Department of Mechanical and Industrial Engineering
University of Toronto
Toronto, Ontario, Canada, M5S 3G8
Email: carlos.dasilva@utoronto.ca

ABSTRACT

Despite the extensive research done on two-dimensional materials in recent years, little is still known about the physics of thermal energy carriers (phonons) at this low dimensionality, especially when these materials are stretched. In this work, we apply molecular dynamics simulations to estimate phonon relaxation times and thermal conductivities of strained samples of single-layer graphene, boron nitride, and molybdenum disulfide. Our results reveal that the thermal response of these 2D materials to tensile strain is considerably different, despite the similarities of their lattice structures. On the one hand, the thermal conductivity of boron nitride monotonically increases until 18% of strain is applied, approximately doubling the conductivity of an unstrained sample. On the other hand, the thermal conductivity of graphene first increases by roughly 30% until 8% of strain is applied, and then it sharply decreases for higher percentages of strain. In contrast, the conductivity of molybdenum disulfide drops dramatically in response to percentages of strain as small as 2%. These thermal responses are addressed here in the context of the phonon properties of these materials, with particular emphasis on the role of the acoustic phonon modes.

KEY WORDS: 2D materials, strain, phonons, molecular dynamics, spectral analysis.

NOMENCLATURE

C_{ph}	Phonon heat capacity, J/nm ³ K
K	Thermal conductivity, W/mK
Kb	Boltzmann constant, J/K
N	Number of unit cells
P	Power Spectrum
T	Temperature, K
V	Volume of simulation cell, nm ³
e	Normal mode eigenvector
$\hbar$	Reduced Plank constant, Js
k	Wave vector, nm ⁻¹
m	Atomic mass, a.u.
n	Number of atoms in the unit cell
$\dot{q}$	Time derivative of normal mode coordinates
r_o	Equilibrium atomic position, nm
t_o	Time of Fourier sampling window, ps
v	Phonon group velocity, nm/ps

Greek symbols

ν	Polarization branch
τ	Phonon relaxation time, ps
ω	Phonon frequency, rad/ps

Subscripts

b	Atom identifier
l	Unit cell identifier
α	Cartesian component

INTRODUCTION

Among the hundreds of 2D materials that have been successfully synthesized in recent years, graphene, boron nitride, and molybdenum disulfide are the ones that have been intensively studied. Recent studies demonstrate that these materials exhibit thermal conductivities significantly higher than those of bulk samples of the same material [1]. However, little is known about the propagation and scattering of phonons at this low dimensionality, especially when atomistic defects and strain are present. Strain effects have been extensively studied in bulk materials [2]. Phonons are known to be ‘stiffened’ when compressive strain is applied, increasing the thermal conductivity [3,4]. In contrast, phonons are known to be ‘softened’ when tensile strain is applied, decreasing the thermal conductivity [3,4]. Phonon dispersion curves change when the material is subjected to strain because the lattice structure is also changed. If the strain is tensile, phonon branches with lower frequencies are obtained, and the contributions of the phonon group velocities to the thermal conductivity are consequentially reduced [3,4]. Another well-known effect of tensile strain in bulk materials is the confinement of energy states in a narrower space, which increases the probability of phonon scattering and then decreases the thermal conductivity [5].

In single-layer materials, the thermal response to strain is different due to the 2D nature of the lattice structure and the unique role of out-of-plane flexural phonon modes [6]. Thus, understanding the physics of phonons in 2D materials is paramount for the development of the next generation of field-effect transistors [7], interconnects [8], composite substrates for power electronics [9], and data storage systems [10]; required for the continued evolution of the information age.

In this work, we investigated the phonon properties and thermal conductivities of strained monolayers of graphene, boron nitride, and molybdenum disulfide. We implemented a robust simulation approach that combine Bose-Einstein statistics, harmonic lattice dynamics (HLD), and molecular dynamics (MD). The main advantage of this approach over other simulation techniques is the treatment of phonons on a mode-by-mode basis. It is noteworthy to mention that most of the MD studies on 2D materials have been conducted at the system level with the Green-Kubo method [11] and Direct method [12], without any insight into the phonon properties.

THERMAL TRANSPORT MODEL

In this work, we extend our simulation approach applied on unstrained samples of 2D materials [6,13] to strained samples of single-layer graphene, boron nitride, and molybdenum disulfide. We apply spectral analysis to a set of MD trajectories to estimate phonon relaxation times, HLD to estimate phonon group velocities, and Bose-Einstein statistics to estimate phonon heat capacities. These phonon properties are used to predict the thermal conductivity using a mode-dependent equation from kinetic theory as

$$K_{\alpha}(k, \nu) = \sum_{k, \nu} C_{ph}(k, \nu) v_{\alpha}^2(k, \nu) \tau(k, \nu), \quad (1)$$

where $C_{ph}(k, \nu)$ is the phonon heat capacity, $v_{\alpha}(k, \nu)$ is the α^{th} component of the phonon group velocity, and $\tau(k, \nu)$ is the phonon lifetime or relaxation time. All phonon properties are functions of the wave vector k and polarization branch ν .

Bose-Einstein Statistics

The thermal conductivities are estimated at room temperature ($T=300K$), well below the Debye temperature (classic limit) in graphene and boron nitride. Quantum effects are significant in 2D materials at room temperature, and applying the equipartition theorem is no longer valid. Therefore, quantum effects are incorporated here by applying Bose-Einstein statistics to estimate heat capacities as

$$C_{ph}(k, \nu) = \frac{Kb x(k, \nu)^2 e^{x(k, \nu)}}{V (e^{x(k, \nu)} - 1)^2} \quad (2)$$

where, Kb is the Boltzmann constant, V is the volume of the simulation sample, and $x(k, \nu) = \hbar \omega(k, \nu) / Kb T$; with $\omega(k, \nu)$ being the phonon frequency, and $\hbar$ the reduced Planck's constant.

Harmonic Lattice Dynamics

We apply HLD calculations to solve the eigenvalue problem for the atoms in the primitive unit cell, obtaining the harmonic phonon frequencies and the phonon mode eigenvectors. We then generate the phonon dispersion curves with these harmonic frequencies and estimate their slopes (phonon group velocities) with central differences. The HLD calculations are conducted with the General Utility Lattice Program (GULP) [14] using empirically approximated interatomic potentials. A Tersoff-type interatomic potential developed by Kinaci et al. [15] is implemented to describe the lattice vibrational properties of single-layer graphene and boron nitride. On the other hand, the vibrational properties of single-layer molybdenum disulfide are described by a Stillinger-Weber-type potential recently developed by Kandemir et al. [16].

Phonon Spectral Energy Density

We use the LAMMPS package [17] to obtain sets of MD atomic velocities that are later post processed using spectral

energy density. First, we use these atomic velocities along with the equilibrium atomic positions and mode eigenvectors to build the time derivative of the normal mode coordinates as

$$\dot{q}(k, \nu, t) = \sum_{l, b, \alpha} \sqrt{\frac{m_b}{N}} \dot{u}_{\alpha}(l, b, t) e^{*}(k, \nu, b, \alpha) \times \exp[ik \cdot r_o(l, b)], \quad (3)$$

where n is the number of atoms in the unit cell, N is the number of unit cells, m_b is the atomic mass of atom b , $\dot{u}_{\alpha}(l, b, t)$ is the α^{th} component of the velocity of atom b in the unit cell l and time instant t , $r_o(l, b)$ is the equilibrium atomic position, and $e^{*}(k, \nu, b, \alpha)$ is the complex conjugate of the eigenvector of atom b in the direction α .

Fast Fourier transform (FFT) is then applied to the autocorrelation of Eq. (3) to generate the power spectrum as

$$P(k, \nu, \omega) = \lim_{t_0 \rightarrow \infty} \frac{1}{2t_0} \left| \frac{1}{\sqrt{2\pi}} \int_0^{t_0} \dot{q}(k, \nu, t) e^{-i\omega t} dt \right|^2, \quad (4)$$

where, t_0 is the time of the Fourier sampling window. The power spectra are averaged over results from four sampling windows and ten independent MD simulations. The phonon relaxation times are calculated from the width at half maximum of the peaks in the power spectra, according to anharmonic theory. Further simulation details are discussed in Refs. [6] and [18].

This simulation approach is applied on strained samples of single-layer graphene, boron nitride, and molybdenum disulfide; of approximately 20nm x 20nm and 15000 atoms. The lattice structures are uniaxially stretched at a constant engineering strain rate of 2.3×10^{-5} 1/ps for 800 ps, which corresponds to a deformation of 2% with a simulation timestep of 0.2 fs. Once the lattice is stretched to the desired level, the structure is allowed to relax in the y direction. Then, atomic velocities are collected to be later post processed. Successive deformation steps of 2% are performed until observing a conclusive trend in the thermal conductivity response.

RESULTS AND DISCUSSIONS

The honeycomb lattice structures of graphene, boron nitride, and molybdenum disulfide are stretched in the x direction in successive steps of 2% of deformation, as shown in Fig. 1 for the lattice structure of boron nitride. For clarity, Fig. 1 shows only three percentages of deformation: 0%, 10%, and 18%. The corresponding thermal responses to all percentages of deformation are shown in Figs. 2, 3, and 4. The in-plane thermal conductivities of all unstrained monolayers (0% strain) are isotropic; however, they become highly anisotropic as the lattices of graphene and boron nitride are stretched. In molybdenum disulfide, the isotropic behavior is preserved and the conductivities in both directions drop dramatically when strain is applied (see Fig. 4).

Fig. 1 Deformation of the lattice structure of boron nitride when uniaxial tensile strain is applied in the x direction. The figure shows three levels of deformation: 0%, 10%, and 20%. Boron atoms are painted in blue and nitrogen atoms in red.

The conductivities of graphene and boron nitride are significantly higher in the stretching direction (x direction). In the y direction, the thermal conductivity decreases at a constant rate of approximately 23 W/mK/strain in graphene, and 10 W/mK/strain in boron nitride. In graphene, the thermal conductivity in the x direction first increases until 8% of strain is applied, and then it decreases for higher percentages. In contrast, the thermal conductivity of boron nitride in the x direction monotonically increases, reaching a plateau at approximately 18% of strain. Investigating the thermal response of boron nitride to higher percentages of strain is necessary to elucidate if a decreasing trend is also observed in this material.

Fig. 2 Variation of the thermal conductivity of graphene with the percentage of deformation applied in the x direction.

It is noteworthy that the maximum increase in boron nitride (~90%) is substantially higher than that predicted in graphene (~30%). These results contrast with those obtained with the Direct method [12], where approximately a 25% maximum increase was predicted in boron nitride and only a 2% maximum increase in graphene. These discrepancies are attributed to the strong effect imposed by the fixed boundaries of the simulation domain in the Direct method, which is aggravated as the thermal conductivity increases because the mean free path of phonons also increases. The phonon transport approach used here is more suitable to study this thermal response in 2D materials because it considers periodic boundary conditions at the boundaries, and it takes into account the quantum effects. Also, it allows to explore the response of

individual phonon modes. The thermal conductivity results presented in this research are expected to be size-dependent. Obtaining size-independent thermal conductivities with the simulation method applied here is prohibited due to the computational cost of the simulations. Therefore, these results cannot be directly compared with available experimental data. Instead, it is recommended to take these thermal conductivities in relative terms and compared them with results from other theoretical approaches.

Fig. 3 Variation of the thermal conductivity of boron nitride with the percentage of deformation applied in the x direction.

Fig. 4 Variation of the thermal conductivity of molybdenum disulfide with the percentage of deformation applied in the x direction.

The mode-by-mode analyses of the phonon properties and thermal conductivities of graphene, boron nitride, and molybdenum disulfide are shown in Figs. 5, 6, and 7, respectively. These results reveal that the anomalous thermal response to tensile strain in 2D layers of graphene and boron nitride is mainly caused by the higher contributions of out-of-plane phonon modes (ZA), which are in turn caused by the linearization of the dispersion curves of ZA modes (higher group velocities) and the increase in lifetimes of low-frequency phonons (up to ~8THz). As shown in Fig. 5e, the maximum thermal conductivity predicted for graphene at 8% of strain (see Fig. 2) is driven by the interplay between the contributions of in-plane acoustic modes (TA and LA) and out-of-plane acoustic modes (ZA). Overall, the increase in lifetimes of low-frequency

phonons also causes a slight increase in the contributions of in-plane acoustic modes up to 8% of strain is applied. However, the contributions of these in-plane modes in graphene drop significantly at percentages of strain higher than 8%, due to the combined effect of smaller group velocities and the reduction in lifetimes of higher-frequency phonons. Figures 5c and 5d show how the lifetimes of TA and LA are reduced in the frequency range 10-26 THz when a 12% of strain is applied.

Figure 6e shows that the contributions of ZA modes in boron nitride also increase significantly when the lattice is stretched; however, the contributions of the in-plane modes remains practical unchanged for percentages of strain higher than 8%. Consequently, the thermal response of boron nitride shown in Fig. 3 does not exhibit an inflection point as the one predicted for graphene, instead it grows monotonically until 18% of strain is applied. It is noteworthy that the relaxation time of higher-frequency phonons (10-26 THz) are not reduced in the same magnitude as those in graphene, instead they are practically unaffected by the application of strain. In addition, it is also relevant to highlight that the group velocities of TA moves (see Fig. 6a) slightly increase when the structure is stretched in the x direction.

The response of ZA modes in molybdenum disulfide diverges significantly from those of graphene and boron nitride, as shown in Fig. 7e. In this case, the contributions of all in-plane phonon modes are consistently reduced when the lattice is subjected to different percentages of strain. This response is caused by the reduction of both group velocities and relaxation

times, which is consistent with the expected response in bulk materials. Single-layer molybdenum disulfide is not strictly two-dimensional because the sulfur atoms are located below and above the molybdenum atoms, creating a quasi-two-dimensional lattice structure. The unique response of ZA modes in graphene and boron nitride is not observed in molybdenum disulfide because the out-of-plane scattering mechanisms are not absent in the quasi-two-dimensional lattice.

Summary & Conclusions

In this work, the thermal responses of single-layer graphene, boron nitride, and molybdenum disulfide were investigated from a phonon transport perspective. The mode-by-mode analysis reveals that the thermal conductivities of these materials respond differently when their lattices are subjected to tensile strain, despite the similarities of their lattice structures. On the one hand, the thermal conductivity of boron nitride monotonically increases until a 18% of strain is applied, approximately doubling the conductivity of an unstrained sample. On the other hand, the thermal conductivity of graphene first increases by approximately 30% until 8% of strain is applied, and then it sharply decreases for higher percentages of strain. In contrast, the conductivity of molybdenum disulfide drops dramatically in response to percentages of strain as small as 2%. These thermal responses were addressed in the context of the phonon properties, with particular attention on the role of the acoustic phonon modes.

Fig. 5 (a) Acoustic dispersion curves of graphene along the k-space direction [1 0 0] for three percentages of uniaxial tensile strain: 0%, 6%, and 12%. Response of the phonon lifetime distribution of graphene to the application of strain for (b) the ZA modes, (c) TA modes, and (d) LA modes. (e) Variation of the thermal conductivity contributions of the acoustic modes of graphene with the percentage of deformation applied in the x direction.

Fig. 6 (a) Acoustic dispersion curves of boron nitride along the k-space direction [1 0 0] for three percentages of uniaxial tensile strain: 0%, 6%, and 12%. Response of the phonon lifetime distribution of boron nitride to the application of strain for (b) the ZA modes, (c) TA modes, and (d) LA modes. (e) Variation of the thermal conductivity contributions of the acoustic modes of boron nitride with the percentage of deformation applied in the x direction.

Fig. 7 (a) Acoustic dispersion curves of molybdenum disulfide along the k-space direction [1 0 0] for three percentages of uniaxial tensile strain: 0%, 6%, and 12%. Response of the phonon lifetime distribution of molybdenum disulfide to the application of strain for (b) the ZA modes, (c) TA modes, and (d) LA modes. (e) Variation of the thermal conductivity contributions of the acoustic modes of molybdenum disulfide with the percentage of deformation applied in the x direction.

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