THERMAL TRANSPORT IN GRAPHENE-BASED NANOSTRUCTURES AND OTHER TWO-DIMENSIONAL MATERIALS

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DISSESSATION

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ABSTRACT

Heat conduction in nanomaterials is an important area of study, with both fundamental and technological implications. However, little is known about heat flow in two-dimensional (2D) materials or devices with dimensions comparable to the phonon mean free path (MFP). Here, we investigated thermal transport in graphene-based nanostructures and several other 2D materials.

First, we measured heat conduction in nanoscale graphene by a substrate-supported thermometry platform. Short, quarter-micron graphene samples reach ~35% of the ballistic thermal conductance limit ($G_{\text{ball}}$) up to room temperature, enabled by the relatively large phonon MFP (~100 nm) in SiO$_2$ substrate-supported graphene. In contrast, patterning similar samples into nanoribbons leads to a diffusive heat flow regime that is controlled by ribbon width and edge disorder. These results show how manipulation of device dimensions on the scale of the phonon MFP can be used to achieve full control of their heat-carrying properties, approaching fundamentally limited upper or lower bounds.

We also examined the possibility of using this supported platform to measure other materials through finite element simulations and uncertainty analysis. The smallest thermal sheet conductance that can be sensed by this method within a 50% error is ~25 nW K$^{-1}$ at room temperature, indicating this platform can be applied to most thin films like polymer and nanotube networks, as well as nanomaterials like nanotube or nanowire arrays, even a single Si nanowire. Moreover, the platform can be extended to plastic substrates, not limited to the SiO$_2$/Si substrate.

Last, we calculated in-plane (for monolayer and bulk) and cross-plane (for bulk) ballistic thermal conductances $G_{\text{ball}}$ of graphene/graphite, $h$-BN, MoS$_2$, and WS$_2$, based on full phonon dispersions from first-principles approach. Then, a rigorous and proper average of phonon mean free path, $\lambda$ was simply obtained in terms of $G_{\text{ball}}$ and the diffusive thermal conductivity. Moreover, length-dependent thermal conductivity ($k$) was estimated using a ballistic-diffusive model, which agrees with available experimental data and shows increasing $k$ with length until $\sim100\lambda$ before convergence. This indicates that, to observe theoretically predicted $k$ divergence in low-dimensional systems, simulations and experiments should extend beyond length $\sim100\lambda$.

Our work provides a comprehensive study of thermal conduction in 2D layered materials in micro- and nanoscale with an emphasis on ballistic conduction and size effects. The findings extend our understanding of thermal conduction and how to tune it to reach the requirements for potential applications like thermal management and thermoelectric conversion.
To my parents
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CHAPTER 1
INTRODUCTION

1.1 Power Dissipation and Thermal Management

In today’s information technology (IT) era, demands for power usage in electronics are growing exponentially, and power dissipation has been a big issue in energy consumption. Taking the United States as an example, the total IT power use in 2007 was estimated to be ~20.6 gigawatts (GW), where the biggest usage is from data centers (~7 GW) [1], as shown in Fig. 1.1a. The power usage in US data centers continuously increases year-by-year, and has been tripled from 2000 to 2011 (Fig. 1.1b) [1]. Figure 1.1a also shows that the power usage by work and home personal computers (PCs) is significant high as well. These issues of power dissipation are due to increased power density in microprocessor (CPUs) when the transistor size is scaled down following the Moore’s law. Figure 1.2 shows that the typical CPU power density increased exponentially over time and flattened out after 2004 when it reached ~100 W/cm² due to the introduction of multi-core CPUs [1]. This power density is approximately an order of magnitude higher than that of a hot plate, implying incredible heat generated in devices. This is clearly

FIG. 1.1: (a) Estimate of US total IT power use in 2007. (b) Estimate of US data center power use from 2000 to 2011. Adapted from Ref. [1].
reflected in the power usage of US data centers, where about half of it is used for cooling.

To accommodate the increasing power dissipation, measures must be taken to ensure that the generated waste heat is properly managed. One strategy of managing this waste heat is to modify the design of the transistor and its surrounding packaging, and to use thermally conductive materials which can help to transport heat away from regions of localized Joule heating. Another strategy is to use thermoelectric materials with low thermal conductivity to convert extra heat to electrical power [2, 3]. Both require effective control of thermal conduction ability in materials, which relies on comprehensive and deep understanding of thermal transport [4, 5].

![Graph showing power density vs. time for computer processors](image)

**FIG. 1.2**: Power density vs. time for computer processors manufactured by AMD, Intel, and Power PC over the past two decades. The exponential trend in power density, although flattened by the introduction of multi-core CPUs, is a limiting factor for the future scaling of semiconductor technology. Adapted from Ref. [1].

### 1.2 Two-Dimensional Materials

As an ultimately two-dimensional (2D) crystal, graphene, an atomic single-layer of graphite (Fig. 1.3a), has attracted huge research attention since its discovery in 2004 [6]. It has unique band structure with a linear dispersion relation near the Brillouin corner (Dirac point), leading to tunable electron and hole doping [7, 8]. Graphene thus exhibits extraordinary electronic and
optical properties like high carrier mobility ~$10^4\ \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and optical transparency, and presents promising applications in electronics, optoelectronics, and photonics [9-15]. A drawback of graphene is the absence of a band gap, which leads to low on/off ratios in transistor performance.

Stimulated by the extensive studies of graphene, other 2D materials start to be fabricated and investigated. For example, hexagonal boron nitride ($h$-BN, see Fig. 1.3b) is a 2D insulator (band gap ~5 eV) and serves as the best dielectric substrate for graphene, because it reduces surface roughness compared to other substrates like SiO$_2$ [16]. In addition, transition metal dichalcogenides (TMDs, with the form of MX$_2$: M = transition metal, and X = S, Se, or Te) can be exfoliated into 2D layers (Fig. 1.3c), and they are mostly semiconductors. Among them, 2D molybdenum disulfide MoS$_2$ was first achieved in experiments and shown a high on/off ratio of ~$10^8$ when used as transistors [17], due to the presence of a band gap ~1.8 eV [18, 19].

These 2D materials can be used independently or further assembled layer-by-layer into van der Waals (vdW) heterostructures [20] (Fig. 1.3d), which widens their potential applications like hetero-junctions and tunneling devices. However, compared to extensive studies of the electrical

**FIG. 1.3:** Schematic structures of (a) graphene [8], (b) single layer of hexagonal boron nitride, and (c) single layer of transition-metal dichalcogenides MX$_2$ [17], where M is transition metal, and X is chalcogen atoms. (d) Schematic of vdW heterostructure assembled by graphene, h-BN, MoS$_2$, and WSe$_2$ [20].
and optical properties of these 2D materials, our understanding of their thermal properties is relatively lacking, especially for micro and nanoscale in which these materials are used for devices [21-24]. Their thermal properties inevitably affect heat dissipation in devices, and hence should be systematically and carefully investigated to understand new physics in micro and nanoscale as well as explore possible applications in thermal management and thermoelectric energy conversion.

1.3 Organization of Dissertation

In this dissertation, we investigated thermal transport in graphene and several other 2D layered materials, with a focus on nanoscale ballistic conduction and size effects. This dissertation is a combination of experiments, finite element simulations, and theoretical calculations.

In Chapter 2, we briefly reviewed experimental studies on thermal and thermoelectric properties of graphene, including up-to-date experimental methods, intrinsic and extrinsic thermal conductivity, interface thermal conductance, and thermoelectric power.

In Chapter 3, we measured thermal conduction in SiO$_2$-supported graphene and graphene nanoribbons by the substrate-supported thermometry platform. Quasi-ballistic thermal conduction was observed in quarter-micron long graphene up to room temperature. Graphene nanoribbons show clear width-dependent thermal conductivity due to phonon scattering with edge disorder.

In Chapter 4, we discussed the applicability of the substrate-supported thermometry platform to other materials, based on finite element simulations. We estimated the lower limit of the measurable thermal sheet conductance by this method, and demonstrated it can be used to measure most thin films and some nanomaterials like nanotube/nanowire arrays, even a single nanowire.
In Chapter 5, we calculated the ballistic thermal conductances of graphene, $h$-BN, MoS$_2$, and WS$_2$ (including their monolayers and bulk) based on full phonon dispersions. From obtained ballistic thermal conductance, we estimated their average phonon mean free paths and length-dependent thermal conductivity due to ballistic-diffusive transition.

In Chapter 6, we conclude the dissertation with a summary of key findings and discussions of possible future directions.
CHAPTER 2

REVIEW OF THERMAL AND THERMOELECTRIC PROPERTIES OF GRAPHENE*

Since graphene is a single atomic layer of graphite, its thermal properties can be understood from those of graphite. Figure 2.1a shows the atomic structure of the typical AB (i.e., Bernal) stacking of graphene layers in graphite. The adjacent carbon atoms within one layer are connected by strong covalent \(sp^2\) bonds with a bonding energy of approximately 5.9 eV [27]. In contrast, the adjacent graphene layers are stacked via weak van der Waals interactions (~50 meV) [27].

The lattice vibrational modes (phonons) of graphene, directly related to its thermal properties, are described by the phonon dispersion in the Brillouin zone, as shown in Fig. 2.1b. Due to \(N = 2\) carbon atoms in graphene unit cell, the dispersion contains 3 acoustic (A) and \(3N-3 = 3\) optical (O) phonon modes. Besides the usual longitudinal (L) and transverse (T) modes, the unique 2D nature of graphene leads to flexural (Z) phonon modes, corresponding to out-of-plane atomic

FIG. 2.1: (a) Schematic of atomic arrangement in graphene sheets [23]. Dashed lines in the bottom sheet represent the outline of the unit cell. (b) Calculated phonon dispersions along high-symmetry lines for monolayer graphene, where red circles [25] and blue triangles [26] are experimental data plotted for comparison. Inset is the Brillouin zone of graphene.

displacements. At low phonon wave vector $q$, the TA and LA modes have linear dispersions of $\omega_{TA} \approx v_{TA}q$ and $\omega_{LA} \approx v_{LA}q$, where $v_{TA} \approx 14$ km/s and $v_{LA} \approx 21$ km/s [28]. These group velocities are 4-6 times higher than those in Si or Ge due to the strong in-plane $sp^2$ bonds and small mass of carbon atoms [23]. Whereas, ZA modes show an approximately quadratic dispersion, $\omega_{ZA} \approx \alpha q^2$ with $\alpha \approx 6.2 \times 10^{-7}$ m$^2$/s [29].

2.1 Methods to Measure Thermal Conductivity

Thermal conduction through a solid material is usually modeled on the basis of Fourier's law that relates the local heat flux $J$ to the local temperature gradient $\nabla T$: $J = -k \nabla T$, where $k$ is the thermal conductivity and has the units of [Wm$^{-1}$K$^{-1}$]. The minus sign in front of $k$ implies that heat flows in the direction opposite to that of the temperature gradient i.e., heat flows from the hotter to the colder regions of the solid.

Measuring nanoscale thermal transport is quite challenging due to high requirements of sample fabrication and temperature sensing [30, 31]. So far, methods used to probe thermal conduction in graphene include optothermal Raman thermometry [32-43], thermoreflectance technique [44-47], 3ω method [48], micro-resistance thermometry [49-57], electrical self-heating method [58, 59], and scanning thermal microscopy (SThM) [60-62]. Here we mainly discuss and compare two techniques widely used to measure in-plane thermal conductivity of graphene, i.e., optothermal Raman thermometry and micro-resistance thermometry.

2.1.1 Optothermal Raman Thermometry

The optothermal Raman thermometry technique was developed to measure suspended, micrometer scale ($> 2 \mu m$) graphene. A laser light was focused at the center of the suspended graphene flake to generate a heating power $P_H$ and raise temperature locally (Figs. 2.2a-b). Meanwhile, the Raman spectrum of graphene was recorded and the temperature rise $\Delta T$ could be
monitored by calibrating it with Raman G peak position [32-36], 2D peak position [37-40] (only for monolayer), or Stokes/anti-Stokes ratio [41, 42]. By knowing the correlation between $P_H$ and $\Delta T$, as well as the geometry size of suspended graphene, its in-plane thermal conductivity $k$ can be extracted through the solution of the heat diffusion equation. The early experiments [32-35] were carried out on graphene strips suspended over a trench (Fig. 2.2a). This was modified in subsequent experiments [36-41], by adopting circular holes with graphene over them (Fig. 2.2b), which matches with the radial symmetry of the laser spot and allowed for an analytic solution of the temperature distribution [22].

**FIG. 2.2:** (a) Schematic of the optothermal Raman thermometry set-up, where a graphene strip is suspended over a trench and heated up by a focused laser light [34]. (b) Schematic of the Raman thermometry set-up with addition of a laser power meter to measure optical transmittance. Inset is the Raman G peak map of graphene suspended over a circular hole [36]. (c) Scanning electron microscopy (SEM) image of micro-resistance thermometry device with SLG supported on a suspended SiO$_2$ membrane between thermometers [49]. Scale bar is 3 $\mu$m. (d) Optical image of bilayer graphene (BLG) suspended over two thermometer pads [53]. Scale bar is 10 $\mu$m. (e) SEM image of a SiO$_2$/Si-supported micro-resistance thermometry device to measure encased few-layer graphene (FLG) [54]. (f) False-colored SEM image of a GNR array on SiO$_2$/Si with micro-resistance thermometers. Inset is a zoom-in atomic force microscopy (AFM) image of GNRs [55].
A major source of uncertainty in different works using the Raman thermometry technique is determining the laser power absorbed by graphene, that is, determining optical absorbance of graphene. Balandin et al. [33] and Ghosh et al. [32, 34, 35] evaluated this number by comparing the integrated Raman G peak intensity of graphene with that of highly oriented pyrolytic graphite (HOPG), leading to ~9% if converted to optical absorbance for exfoliated single-layer graphene (SLG) [22]. The measured value of ~9% considered two passes of light (down and reflected back) and resonance absorption effects due to close proximity of graphene to the substrate, and corresponded to 488-nm wavelength where absorption is higher than the 2.3% long-wavelength limit [63]. Faugeras et al. [41], Lee et al. [37], and Vlassiouk et al. [42] did not measure the optical absorbance under the conditions of their experiments and assumed a value of 2.3% for exfoliated SLG based on a separate optical transmission measurement [63]. Cai et al. [36] and Chen et al. [38] obtained values of 3.3±1.1% and 3.4±0.7% for CVD SLG by directly measuring the optical transmittance via addition of a power meter under the suspended portion of graphene (Fig. 2.2b). The used optical absorbance is very important because it would proportionally change extracted $k$. We note that both theory [64] and experiments [65-67] showed an increase of optical absorbance in graphene with decreasing laser wavelength due to many-body effect, and the values of Cai et al. [36] and Chen et al. [38] are consistent with those experimental results. To obtain reliable $k$, it is thus necessary to measure optical absorbance under used laser wavelength and specific experimental conditions.

Another uncertainty source is the calibration of temperature with features of Raman spectrum. It is known that strains and impurities in graphene can affect the Raman peak positions and their temperature dependence [68], which greatly limits the temperature sensitivity of the Raman thermometry technique. In addition, heat loss from graphene to the surrounding air was neglect-
ed in most experiments, but Chen et al. [38] found that for a large diameter \(9.7 \mu \text{m}\) graphene flake, the \(k\) obtained in air could be overestimated by 14–40\% compared with the value obtained in vacuum. This implies measurable errors in previous experiments, even though the influence might be weaker due to smaller sizes of measured graphene. Furthermore, extra uncertainty could come from the difference in \(k\) between suspended and supported portions of graphene, as well as thermal boundary resistance between graphene and supporting substrates [36]. Overall, the Raman thermometry technique provides an efficient way to measure \(k\) of suspended graphene with benefits of relatively easy sample fabrication, reduced graphene contamination, and simple data analysis, but it inevitably has limitations: (i) relatively large uncertainty (up to 40\%) [21]; (ii) difficulty to probe the low temperature regime due to significant heating in graphene by laser; (iii) inability to be applied to nanometer scale or supported graphene, where edge and interface will take effect.

2.1.2 Micro-Resistance Thermometry

The micro-resistance thermometry technique is a steady-state method to directly probe heat flows in materials [30]. It is able to measure both suspended and supported graphene, as well as at the nanometer scale and in low temperature range, with high resolution of temperature by employing electrical resistance as thermometers. This technique can be further divided into two kinds: suspended bridge platform and fully substrate-supported platform. The former was developed by Shi et al. [69, 70] to measure thermal conductivity of 1D nanostructures, and it has been widely used for nanotubes [71-76] and nanowires [77-81]. By using this platform, graphene can be either supported by a suspended \(\text{SiO}_2/\text{SiN}_x\) membrane connecting two thermometers [49-52] (Fig. 2.2c) or fully suspended over two thermometer pads [51, 53, 57] (Fig. 2.2d), enabling measurements of both suspended and supported graphene. The fully substrate-supported plat-
form was developed by Jang et al. [54] and Bae et al. [55], where at least two thermometers were patterned on Si/SiO$_2$-supported graphene (Fig. 2.2e) or GNRs (Fig. 2.2f). In both platforms, one thermometer serves as the heater to generate heating power $P_H$ and a temperature gradient across graphene by electrical heating, meanwhile all thermometers (including the heater) monitor temperature changes $\Delta T$ in terms of their electrical resistance changes. Then, the thermal conductance/conductivity of measured materials can be extracted in a simple analytic way by solving its equivalent thermal resistance circuit for the suspended bridge platform [69, 70], while a complicated 3D numerical (finite element) simulation has to be performed for the substrate-supported platform due to significant heat leakage into the substrate [54, 55].

Although the data extraction of the suspended bridge platform is easier than that of the substrate-supported platform, as a trade-off the sample fabrication is more complicated for the former than the latter. Thus, for materials which are hard to be suspended, such as GNRs, the latter is an advantageous method to be employed. However, the measurable length of interested materials cannot be longer than a few micrometer for the substrate-supported platform, because the temperature drops nearly exponentially away from the heater, leading to undetectable $\Delta T$ if other thermometers are far away. It is worth noting that for the platform of graphene supported by a suspended membrane (Fig. 2.2c) and the substrate-supported platform (Figs. 2.2e and 2.2f), a control experiment has to be carried out by etching off graphene/GNRs and repeating measurements to calibrate the background heat flow and thermal contact resistance between graphene and thermometers [49, 50, 54, 55]. This improves the measurement accuracy. Whereas, for the platform of graphene fully suspended (Fig. 2.2d) such a control experiment cannot be performed, so the thermal contact resistance could be a main source of uncertainty in results. Overall, the micro-resistance thermometry technique has very high resolution of temperature ($<50$ mK) [21,
and can cover a wide temperature range. It can probe both suspended and supported graphene, as well as in nanometer scale. However, attention should be paid to micro/nanofabrication, which could introduce contaminations (like residues and defects) and increase the uncertainty [53].

2.2 Intrinsic Thermal Conductivity of Graphene

In this section, we mainly discuss the “intrinsic” thermal conductivity of SLG based on experimental results and theoretical analysis. Here, by “intrinsic” we mean isolated, large scale, pristine graphene without suffering impurity, defect, interface, and edge scatterings, so its thermal conductivity is only limited by intrinsic phonon-phonon scattering due to crystal anharmonicity [21] and electron-phonon scattering. In experiments, suspended, micrometer scale graphene samples have properties close to intrinsic ones. We thus first summarize current experimental observations of $k$ in suspended SLG.

Using the Raman thermometry technique described above, suspended micro-scale graphene flakes obtained by both exfoliation from graphite [32-35, 37, 41] and CVD growth [36, 38-40, 42] have been measured at room temperature and above. Some representative data versus temperature from these studies are shown in Fig. 2.3a. The obtained in-plane thermal conductivity values of suspended SLG generally fall in the range of $\sim$2000-4000 Wm$^{-1}$K$^{-1}$ at room temperature, and decrease with increasing temperature, reaching about 700-1500 Wm$^{-1}$K$^{-1}$ at $\sim$500 K. The variation of obtained values could be attributed to different choices of graphene optical absorbance (see Section 2.1), thermal contact resistance, different sample geometries, sizes, and qualities. For comparison, we also plot the experimental thermal conductivity of diamond [82], graphite [82], and carbon nanotubes (CNTs) [71, 83] in Fig. 2.3a.
It is clear that suspended graphene has thermal conductivity as high as these carbon allotropes near room temperature, even higher than its 3D counterpart, graphite, whose highest record of observed in-plane $k$ in HOPG is $\sim 2000 \text{Wm}^{-1}\text{K}^{-1}$ at 300 K. The presently available data of graphene based on the Raman thermometry technique only cover the temperature range of $\sim 300$-$600$ K, except one at $\sim 660$ K reported by Faugeras et al. [41] showing $k \approx 630 \text{Wm}^{-1}\text{K}^{-1}$.

For higher temperature, Dorgan et al. [58] used the electrical breakdown method for thermal conductivity measurements and found $k \approx 310 \text{Wm}^{-1}\text{K}^{-1}$ at 1000 K for suspended SLG.

**FIG. 2.3:** (a) Experimental thermal conductivity $k$ as a function of temperature $T$: representative data for suspended CVD SLG by Chen et al. [38] (solid red square), suspended exfoliated SLG by Lee et al. [37] (solid purple asterisk) and Faugeras et al. [41] (solid brown pentagon), suspended SLG by Dorgan et al. [58] (solid grey hexagon), supported exfoliated BLG by Pettes et al. [53] (solid orange diamond), supported exfoliated SLG by Seol et al. [49] (solid black circle), supported CVD SLG by Cai et al. [36] (solid blue right-triangle), encased exfoliated 3-layer graphene (3LG) by Jang et al. [54] (solid cyan left-triangle), supported exfoliated GNR of $W \approx 65$ nm by Bae et al. [55] (solid magenta square), type IIa diamond [82] (open gold diamond), graphite in-plane [82] (open blue up-triangle), graphite cross-plane (open blue down-triangle), suspended single-walled CNT (SWCNT) by Pop et al. [83] (open dark-green circle), and multi-walled CNT (MWCNT) by Kim et al. [71] (solid light-green circle). (b) Thermal conductance per unit cross-sectional area, $G/A = k/L$, converted from thermal conductivity data in (a), compared with the theoretical ballistic limit of graphene (solid line), which can be approximated analytically as $G_{\text{ball}}/A \approx \left[1/(4.4 \times 10^{5}T^{1.68}) + 1/(1.2 \times 10^{10})\right]^{-1}$ $\text{Wm}^{-2}\text{K}^{-1}$ over the temperature range 1–1000 K [55]. Data in (a) whose sample $L$ is unknown or not applicable are not shown in (b).
overall trend of present graphene data from 300 K to 1000 K shows a steeper temperature
dependence than graphite (see Fig. 2.3a), consistent with the extrapolation of thermal conductiv-
ity by Dorgan et al. [58]. This behavior could be attributed to stronger second-order three-phonon
scattering \( (\tau \sim T^{-2}) \) in graphene than graphite enabled by the flexural (ZA) phonons of suspended
graphene [84], similar to the observations in CNTs [83, 85]. For temperature below 300 K, the
micro-resistance thermometry technique needs to be employed for \( k \) measurements. Unfortunat-
ely, there is no reliable data for suspended single-layer graphene until now. However, data do
exist for suspended few-layer graphene (FLG) [51, 53, 56], which will be discussed in Section
2.3.4. It is instructive to compare experimental results with the ballistic limit of graphene as a
check, so we convert measured \( k \) in Fig. 2.3a to thermal conductance per unit cross-sectional area,
\( G/A = k/L \), which are re-plotted in Fig. 2.3b with graphene \( G_{\text{ball}}/A \) (discussed in the next section).

Above room temperature, measured \( G/A \) of suspended SLG are more than one order of magni-
tude lower than \( G_{\text{ball}}/A \), indicating the diffusive regime. The reason that the value of Faugeras et
al. [41] is much lower than others is because of a much larger \( L = 22 \, \mu \text{m} \) (radius) of their sus-
pended graphene.

### 2.3 Extrinsic Thermal Conductivity of Graphene

The long phonon MFP in pristine graphene would suggest that it is possible to tune thermal
conductivity more effectively by introducing extrinsic scattering mechanisms which dominate
over intrinsic scattering mechanisms in graphene. For example, isotope scattering, normally
unimportant with respect to other scattering processes, could become significant in graphene
thermal conduction. It could be easier to observe size effects on thermal transport in graphene
because samples do not have to be extremely shrunk. In the following, we discuss various
scattering mechanisms and their influences on thermal conduction separately, giving rise to
tunable extrinsic thermal conductivity of graphene.

2.3.1 Isotope Effects

The knowledge of isotope effects on thermal transport properties is valuable for tuning heat conduction in graphene. Natural abundance carbon materials are made up of two stable isotopes of $^{12}$C (98.9%) and $^{13}$C (1.1%). Changing isotope composition can modify dynamic properties of crystal lattices and affect their thermal conductivity [89, 90]. For instance, it has been found that at room temperature isotopically purified diamond has a thermal conductivity of $\sim$3300 Wm$^{-1}$K$^{-1}$ [91, 92], about 50% higher than that of natural diamond, $\sim$2200 Wm$^{-1}$K$^{-1}$ [82]. Similar effects have also been observed in 1D nanostructures, boron nitride nanotubes [73]. Very recently, the first experimental work to show the isotope effect on graphene thermal conduction was reported by Chen et al. [39]. By using the CVD technique, they synthesized isotopically modified graphene containing various percentages of $^{13}$C. The graphene flakes were subsequently suspended over 2.8-µm-diameter holes and thermal conductivity was measured by the Raman thermometry.

**FIG. 2.4:** (a) Thermal conductivity of suspended CVD graphene as a function of temperature for different $^{13}$C concentrations, showing isotope effect [39], b) Thermal conductivity of suspended CVD graphene with (red down-triangle) and without (blue up-triangle) wrinkles as a function of temperature. Also shown in comparison are the literature thermal conductivity data of pyrolytic graphite samples [86-88]. Inset shows the SEM image of CVD graphene on the Au-coated SiNx holey membrane. The red arrow indicates a wrinkle. Scale bar is 10 µm [40].
technique. As shown in Fig. 2.4a, compared with natural abundance graphene (1.1% $^{13}$C), the $k$ values were enhanced in isotopically purified samples (0.01% $^{13}$C), and reduced in isotopically mixed ones (50% $^{13}$C).

2.3.2 Structural Defect Effects

Structural defects are common in fabricated graphene, especially in CVD grown graphene [93, 94]. The effects of wrinkles [40] and grain size [42] on the thermal conduction of suspended single-layer CVD graphene have been examined in experiments by using the Raman thermometry technique. Chen et al. [40] found that the thermal conductivity of graphene with obvious wrinkles (indicated by arrows in the inset of Fig. 2.4b) is about 15-30% lower than that of wrinkle-free graphene over their measured temperature range, ~330-520 K (Fig. 2.4b). Vlassiouk et al. [42] measured suspended graphene with different grain sizes obtained by changing the temperature of CVD growth. The grain sizes $\ell_G$ were estimated to be 150 nm, 38 nm, and 1.3 nm in different samples in terms of the intensity ratio of the G peak to D peak in Raman spectra [95]. Since grain boundaries in graphene serve as extended defects and scatter phonons, graphene with smaller grain sizes are expected to suffer more frequent phonon scattering. Their measured thermal conductivity does show a decrease for smaller grain sizes, indicating the observation of the grain boundary effect on thermal conduction. Whereas, the dependence on the grain size shows a weak power law, $k \sim \ell_G^{1/3}$, for which there is no theoretical explanation yet [42]. However, for SiO$_2$-supported graphene, recent theoretical work based on NEGF method showed a similar but stronger dependence of $k$ on the grain size $\ell_G$ in the range of $\ell_G < 1$ µm [96]. Further experimental studies are required to reveal the grain size effects on the thermal transport of both suspended and supported graphene.

2.3.3 Substrate Effects in Supported Graphene
For practical applications, graphene is usually attached to a substrate in electronic and optoelectronic devices, so it is important to understand substrate effects on thermal properties of supported graphene [97-100]. Seol et al. [49, 50] measured exfoliated SLG on a 300 nm thick SiO$_2$ membrane by using the micro-resistance thermometry technique with the suspended bridge platform (Fig. 2.2c). The observed thermal conductivity is $k \sim 600$ Wm$^{-1}$K$^{-1}$ near room temperature (solid black circles in Fig. 2.3a). This value is much lower than those reported for suspended SLG via the Raman thermometry technique, but is still relatively high compared with those of bulk silicon ($\sim 150$ Wm$^{-1}$K$^{-1}$) and copper ($\sim 400$ Wm$^{-1}$K$^{-1}$). Another study by Cai et al. [36] showed CVD SLG supported on Au also has a decreased thermal conductivity, $\sim 370$ Wm$^{-1}$K$^{-1}$ (this lower value compared to $\sim 600$ Wm$^{-1}$K$^{-1}$ could be caused by grain boundary scattering in CVD graphene [96]). The thermal conductivity reduction in supported graphene is attributed to substrate scattering, which strongly affects the out-of-plane flexural (ZA) mode of graphene [49, 97, 101]. This effect becomes stronger in encased graphene, where graphene is sandwiched between bottom and top SiO$_2$. The thermal conductivity of SiO$_2$-encased exfoliated SLG was measured to be below 160 Wm$^{-1}$K$^{-1}$, reported by Jang et al. [54] using the micro-resistance thermometry technique with the substrate-supported platform (Fig. 2.2e). For encased graphene, besides the phonon scattering by bottom and top oxides, the evaporation of top oxide could cause defects in graphene, which can further lower thermal conductivity. Knowing encased graphene $k$ is useful for analyzing heat dissipation in top-gated graphene devices.

2.3.4 Interlayer Effects in Few-Layer Graphene

Interlayer scattering as well as top and bottom boundary scattering could take place in few-layer graphene, which could be another mechanism to modulate graphene thermal conductivity. It is interesting to investigate the evolution of the thermal conductivity of FLG with increasing
thickness, denoted by the number of atomic layers ($N$), and the critical thickness needed to recover the thermal conductivity of graphite.

Several experimental studies on this topic have been conducted for encased [54], supported [52], and suspended FLG [35, 56], and their results are summarized in Fig. 2.5. Jang et al. [54] measured the thermal transport of SiO$_2$-encased FLG by using the substrate-supported, micro-resistance thermometry platform (Fig. 2.2e). They found that the room-temperature thermal conductivity increases from ~50 to ~1000 Wm$^{-1}$K$^{-1}$ as the FLG thickness increases from 2 to 21 layers, showing a trend to recover natural graphite $k$. This strong thickness dependence was explained by the top and bottom boundary scattering and disorder penetration into FLG induced by the evaporated top oxide [54]. Very recently, another similar yet less pronounced trend was observed in SiO$_2$-supported FLG by Sadeghi et al. [52] using the suspended micro-resistance

![FIG. 2.5: Experimental in-plane thermal conductivity near room temperature as a function of the number of layers $N$ for suspended graphene by Ghosh et al. [35] (open blue diamond) and by Jang et al. [56] (open green square), SiO$_2$-supported graphene by Seol et al. [49] (open red circle and Sadeghi et al. [52] (solid red circle), and SiO$_2$-encased graphene by Jang et al. [54] (solid black triangle). The data show a trend to recover the value (dashed line) measured by Sadeghi et al. [52] for natural graphite source used to exfoliate graphene. The gray shaded area shows the highest reported $k$ values of pyrolytic graphite [86-88]. Adapted from Ref. [52].]
thermometry platform (similar to Fig. 2.2c). As shown by red dots in Fig. 2.5, the measured room-temperature $k$ increases slowly as increasing thickness, and the recovery to natural graphite would occur even more than 34 layers. The difference between the results by Jang et al. [54] and Sadeghi et al. [52] is not unexpected, because encased FLG $k$ could be suppressed much more in thin layers than thick layers due to the effect of top oxide, and hence shows a stronger thickness dependence.

For suspended FLG, there are two contradictory observations in the thickness dependence. At first, based on the Raman thermometry technique (Fig. 2.2a) Ghosh et al. [35] showed a decrease of suspended FLG $k$ from the SLG high value to regular graphite value as thickness increases from 2 to 8 layers (open diamonds in Fig. 2.5). The $k$ reduction was explained by the interlayer coupling and increased phase-space states available for the phonon Umklapp scattering in thicker FLG [35]. However, a very recent study by Jang et al. [56] seems to show a different thickness trend for suspended FLG. They measured thermal conductivity of suspended graphene of 2-4 and 8 layers by using a modified T-bridge micro-resistance thermometry technique. The obtained room-temperature $k$ for 2-4 layers is about 300-400 Wm$^{-1}$K$^{-1}$ with no apparent thickness dependence, while $k$ for 8-layer shows an increase to $\sim$600 Wm$^{-1}$K$^{-1}$ (open squares in Fig. 2.5). Surprisingly, this trend is qualitatively in agreement with that of Sadeghi et al. [52] for supported FLG; both show similar increasing amounts of $k$ from 2 to 8 layers (Fig. 2.5), despite a small decrease from 2 to 4 layers in the former, which could arise from different sample qualities and measurement uncertainty. Given opposite thickness trends of Ghosh et al. [35] and Jang et al. [56], further experimental works are required to clarify the real thickness-dependent $k$ in suspended FLG. Moreover, we want to point out that suspended FLG $k$ values of Jang et al. [56] are close to those reported by Pettes et al. [53] for suspended bilayer graphene (BLG), $\sim$600 Wm$^{-1}$K$^{-1}$.
at room temperature (see Fig. 2.3a). Both are much lower than suspended SLG $k$. The latter attributed this to phonon scattering by a residual polymeric layer on graphene [53], even though the former claimed that electrical current annealing was used to remove polymer residues [56].

### 2.3.5 Cross-Plane Thermal Conduction

A remarkable feature of graphite and graphene is that their thermal properties are highly anisotropic. Despite high thermal conductivity along the in-plane direction, heat flow along the cross-plane direction ($c$-axis) is hundreds of times weaker, limited by weak van der Waals interactions between layers (for graphite) or with adjacent materials (for graphene). For example, the thermal conductivity along the $c$-axis of pyrolytic graphite is only $\sim 6$ Wm$^{-1}$K$^{-1}$ at room temperature [82] (Fig. 2.3a). For graphene, it is often attached to a substrate or embedded in a

**FIG. 2.6:** Experimental thermal interface conductance $G_\perp$ vs. temperature for SLG/SiO$_2$ by Chen et al. [48] (open purple diamond), FLG/SiO$_2$ by Mak et al. [44] (open purple square), CNT/SiO$_2$ by Pop et al. [102] (solid purple right-triangle), Au/SLG by Cai et al. [36] (solid gold diamond), Au/Ti/SLG/SiO$_2$ (solid blue circle) and Au/Ti/graphite (solid orange circle) by Koh et al. [45], interfaces of graphite with Au (solid magenta square), Al (solid gray up-triangle), Ti (solid green asterisk) by Schmidt et al. [103], interfaces of Al/SLG/SiO$_2$ without treatment (open black up-triangle), with oxygen treatment (Al/O-SLG/SiO$_2$, open green up-triangle), and with hydrogen treatment (Al/H-SLG/SiO$_2$, open red up-triangle) by Hopkins et al. [46].
medium for potential applications. Heat conduction along the cross-plane direction is characterized by the thermal interface/boundary conductance between graphene and adjacent materials, which could become a limiting dissipation bottleneck in highly scaled graphene devices and interconnects [23, 104-107].

The thermal interface conductance across graphene/graphite and other materials has been measured by using $3\omega$ method [48], time-domain thermoreflectance (TDTR) technique [44-47, 103, 108], and Raman-based method [36, 43]. Most experimental data available to date are shown in Fig. 2.6, and they are consistent with each other in general, given the variations of sample qualities and measurement techniques. Chen et al. [48] and Mak et al. [44] showed the thermal interface conductance per unit area of graphene/$\text{SiO}_2$ is $G_{\perp} \sim 50$-100 MWm$^{-2}$K$^{-1}$ at room temperature, with no strong dependence on the FLG thickness. Their values are close to that of CNT/$\text{SiO}_2$ [102], reflecting the similarity between graphene and CNT. Schmidt et al. [103] measured $G_{\perp}$ of the graphite/metal interfaces, including Au, Cr, Al, and Ti. Among them, the graphite/Ti has the highest $G_{\perp} \sim 120$ MWm$^{-2}$K$^{-1}$, and the graphite/Au interface has the lowest $G_{\perp} \sim 30$ MWm$^{-2}$K$^{-1}$ near room temperature. Their $G_{\perp}$ of graphite/Au is consistent with the value by Norris et al. [108] and values of SLG/Au by Cai et al. [36] and FLG/Au by Ermakov et al. [43]. Koh et al. [45] later measured heat flow across the Au/Ti/$N$-LG/$\text{SiO}_2$ interfaces with the layer number $N=1$–10. Their observed room-temperature $G_{\perp}$ is $\sim 25$ MWm$^{-2}$K$^{-1}$, which shows a very weak dependence on the layer number $N$ and is equivalent to the total thermal conductance of Au/Ti/graphite and graphene/$\text{SiO}_2$ interfaces acting in series. This indicates that the thermal resistance of two interfaces between graphene and its environment dominates over that between graphene layers. Interestingly, Hopkins et al. [46] showed the thermal conduction across the Al/SLG/$\text{SiO}_2$ interface could be manipulated by introducing chemical adsorbates between the Al.
and SLG. As shown in Fig. 2.6, their measured $G_\perp$ of untreated Al/SLG/SiO$_2$ is $\sim$30 MWm$^{-2}$K$^{-1}$ at room temperature, in agreement with Zhang et al. [47]. The $G_\perp$ increases to $\sim$42 MWm$^{-2}$K$^{-1}$ for oxygen-functionalized graphene (O-SLG), while decreases to $\sim$23 MWm$^{-2}$K$^{-1}$ for hydrogen-functionalized graphene (H-SLG). These effects were attributed to changes in chemical bonding between the metal and graphene, and are consistent with the observed enhancement in $G_\perp$ from the Al/diamond [109] to Al/O-diamond interfaces [110].

### 2.4 Thermoelectric Properties of Graphene

Thermoelectric materials can convert waste heat into electricity by the Seebeck effect and use electricity to drive electronic cooling or heating by the Peltier effect. Thermoelectric devices are all-solid-state devices with no moving parts, thus are silent, reliable and scalable. However, they only find limited applications due to their low efficiency. The efficiency of a thermoelectric material is determined by the thermoelectric figure of merit ($ZT$), which typically is defined as

$$ZT = \frac{\sigma S^2}{k} T$$

where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient [also called thermoelectric power (TEP) or thermopower], $T$ is the absolute temperature, and the thermal conductivity $k = k_e + k_l$ have contributions from electrons ($k_e$) and lattice vibrations ($k_l$). $k_e$ is usually extracted based on the Wiedemann-Franz Law $k_e/\sigma = L_0 T$, where the Lorenz number $L_0$ is equal to $2.44 \times 10^{-8}$ WΩK$^{-2}$ for free electrons. This law does not always hold. For example, $k_e$ becomes zero for a delta-shaped transport distribution [111]. However, in graphene $k_e$ is negligible with respect to $k_l$ [112-116], similar to CNTs [71, 117]. Currently, the state-of-art commercial thermoelectric materials, like Bi$_2$Ti$_3$, have room-temperature $ZT$ around 1 [3].
Thermoelectric transport in graphene has been experimentally investigated in the past five years [118-129]. The Seebeck coefficient $S$ and electrical conductance $G_e$ of graphene can be measured against the gate voltage $V_g$ (thus, carrier density $n_c$) simultaneously via a widely-used microfabricated structure (inset of Fig. 2.7a), which was developed by Small et al. [130] to measure thermoelectric transport in CNTs. Figure 2.7 shows typical results of measured $G_e$ and $S$ as a function of $V_g$ in graphene at different temperatures [118]. The Seebeck coefficient $S$ shows two peaks near the Dirac point (charge neutrality point) and changes its sign across the Dirac point as the majority carrier switches from electron to hole. The room-temperature peak values of $S$ for SLG and BLG are observed to be $\sim$50-100 $\mu$VK$^{-1}$ in different experiments [118-122]. For high carrier density $n_c$ (i.e., high $|V_g|$), the measured Seebeck coefficient scales as $S\sim|n_c|^{1/2}$ for SLG due to its linear dispersion [119], while $S\sim1/|n_c|$ for BLG due to its hyperbolic disper-

FIG. 2.7: (a) Electrical Conductance $G_e$ and (b) thermopower TEP of a graphene sample as a function of back gate voltage $V_g$ for $T = 300$ K (square), 150 K (circle), 80 K (up triangle), 40 K (down triangle), and 10 K (diamond). Upper inset: SEM image of a typical device for thermoelectric measurements, scale bar is 2 $\mu$m. Lower inset: TEP values taken at $V_g = -30$ V (square) and $-5$ V (circle). Dashed lines are linear fits to the data. Adapted from Ref. [118].
sion [121], consistent with theories. Importantly, the simultaneous measurements of $G_e$ and $S$ enable testing the validation of the semiclassical Mott relation [131]:

$$S = -\frac{\pi^2 k_B^2 T}{3e} \left| \frac{dG_e}{dV_g} \right|_{E=E_F}$$

(2.2)

where $k_B$ is the Boltzmann constant, $e$ is the electron charge, and $E_F$ is the Fermi energy. For SLG the measured $S$ shows a linear $T$ dependence (inset of Fig. 2.7b) and matches calculated $S$ from measured $G_e$ by Eq. 2.2 [118-120], indicating an agreement with the Mott relation. For BLG, however, the agreement only holds for high carrier density; for low carrier density there is an obvious difference between measured and calculated $S$ as well as a deviation from the linear $T$ dependence at high temperature [121, 122]. This failure of the Mott relation was attributed to the low Fermi temperature in BLG.

The thermoelectric properties of materials can be also probed by using a conducting tip to measure the thermoelectric voltage between the sample and tip, induced by a given temperature difference between them. By employing atomic force microscopy (AFM) and scanning tunneling microscopy (STM) techniques, Cho et al. [132] and Park et al. [133] measured the thermopower of epitaxial graphene on SiC, respectively. The advantage of this method is the simultaneous imaging of the sample structure and thermoelectric signals with a spatial resolution of atomic-scale. Since the Seebeck coefficient relies on the sample local density of states (LDOS) near the Fermi energy, and LDOS can be quite different in the presence of boundaries and disorders [134-138], thermoelectric imaging allows us to probe grain boundaries, wrinkles, defects, and impurities in graphene, which may not be reflected in topography images [132, 133].

For practical applications, the Seebeck coefficient and power factor $\sigma S^2$ of graphene should be improved. Some experimental efforts have been made in this direction. Wang et al. [121] observed enhanced $S$ below room temperature in a dual-gated BLG device, resulting from the
opening of a band gap by applying a perpendicular electric field on BLG. Additionally, the Seebeck coefficient and power factor of FLG could be enhanced at high temperature (>500 K) by molecular attachments [139] and oxygen plasma treatment [140], attributed to the band gap opening. By constructing the c-axis preferentially oriented nanoscale Sb2Te3 film on monolayer graphene, both S and σ were increased, benefiting from a highway for carriers provided by graphene [141]. From a practical point of view, Hewitt et al. [142] focused on maximizing the power output of FLG/polyvinylidene fluoride composite thin films by considering the absolute temperature, temperature gradient, load resistance, and physical dimensions of films.
CHAPTER 3

BALLISTIC TO DIFFUSIVE CROSSOVER OF HEAT FLOW IN GRA-THENE RIBBONS*

3.1 Introduction

The thermal properties of graphene are derived from those of graphite, and are similarly anisotropic. The in-plane thermal conductivity of isolated graphene is high, \( \approx 2000 \text{ Wm}^{-1}\text{K}^{-1} \) at room temperature, due to the strong sp\(^2\) bonding and relatively small mass of carbon atoms [21, 23, 24, 58]. Heat flow in the cross-plane direction is nearly a thousand times weaker, limited by van der Waals interactions with the environment (for graphene) [45] or between graphene sheets (for graphite) [21, 23]. Recent studies have suggested that the thermal conductivity of graphene is altered when in contact with a substrate through the interaction between vibrational modes (phonons) of graphene and those of the substrate [49, 54, 97, 101]. However an understanding of heat flow properties in nanometer scale samples of graphene [or any other two-dimensional (2D) materials] is currently lacking.

By comparison, most graphene studies have focused on its electrical properties when confined to scales on the order of the carrier mean free path (MFP) [105, 143-149]. For example, these have found that “short” devices exhibit near-ballistic behavior [145], Fabry-Perot wave interference [146], and “narrow” nanoribbons display a steep reduction of charge carrier mobility [144, 147]. Previous studies do exist for heat flow in three-dimensional (3D) structures like nanowires and nanoscale films. For instance, ballistic heat flow was observed in suspended GaAs bridges [150] and silicon nitride membranes [151] at low temperatures, of the order 1 K.

Conversely, suppression of thermal conductivity due to strong edge scattering effects was noted in narrow and rough silicon nanowires [80, 81], up to room temperature. Yet such effects have not been studied in 2D materials like graphene, and ballistic heat conduction has not been previously observed near room temperature in any material.

In this work we find that the thermal properties of graphene can be tuned in nanoscale devices comparable in size to the intrinsic phonon MFP. (By “intrinsic” thermal conductivity or phonon MFP we refer to that in large samples without edge effects, typically limited by phonon-phonon scattering in suspended graphene, and by substrate scattering in supported graphene, here $\lambda \approx 100$ nm at room temperature). The thermal conductance of “short” quarter-micron graphene reaches up to 35% of theoretical ballistic upper limits [96]. However, the thermal conductivity of “narrow” graphene nanoribbons (GNRs) is greatly reduced compared to that of “large” graphene samples. Importantly, we uncover that nanoengineering the GNR dimensions and edges is responsible for altering the effective phonon MFP, shifting heat flow from quasi-ballistic to diffusive regimes. These findings are highly relevant for all nanoscale graphene devices and interconnects, also suggesting new avenues to manipulate thermal transport in 2D and quasi-one-dimensional (1D) systems.

3.2 Experimental Method

3.2.1 Fabrication and Characterization of Graphene Nanoribbons

Graphene monolayers were deposited on SiO$_2$/Si (~290 nm/0.5 mm) substrates by mechanical exfoliation from natural graphite. Graphene thickness and GNR edge disorder were evaluated with Raman spectroscopy [45, 152, 153]. Samples were annealed in Ar/H$_2$ at 400 °C for 40 minutes. We used two approaches to define and fabricate graphene nanoribbon (GNR) arrays with pitch ~150 nm and varying widths: one with a PMMA mask (Fig. 3.1a), the other with an
Al mask (Fig. 3.1b) [154]. Double poly(methyl methacrylate) (PMMA) layers (PMMA 495K A2/PMMA 950K A4) were coated on the Si/SiO$_2$ substrate. For the electron (e)-beam lithography, we used 30 keV e-beam accelerating voltage. After opening 40 nm wide PMMA windows, we etched the graphene exposed through the windows with an oxygen plasma, creating GNRs of width $W$ (Fig. 3.1a). This PMMA mask method was used for the $W \approx 130$ nm, ~85 nm, and ~65 nm wide GNRs. For the narrower ~45 nm GNRs we used Al masks (Fig. 3.1b). In this case, after opening the PMMA windows, instead of plasma etching, we deposited 30 nm thick Al and obtained ~45 nm wide Al strips on graphene. After plasma etching of exposed graphene and Al etching (type A, Transene Company) we obtained ~45 nm wide GNRs. Figure 3.2 shows the atomic force microscopy (AFM) images of fabricated GNR arrays with $W \approx 130$ nm, 85 nm, 65 nm, and 45 nm, respectively. The bottom and top regions of Figs. 3.2a and 3.2c correspond to the un-etched pristine graphene.
To characterize the prepared GNRs, we performed Raman spectroscopy with a 633 nm wavelength laser (~1 µm spot size) as shown in Fig. 3. Even before patterning into GNRs, we selected only monolayer graphene flakes, identifiable through their 2D (G’) to G Raman peak ratio, and through a single fitted Lorentzian to their 2D (G’) peak. The unpatterned graphene samples had no identifiable D peak, indicative of little or no disorder [155]. On the other hand, the GNR arrays showed a pronounced D band consistent with the presence of edge disorder [152]. The peak intensity of the D band with respect to that of the G band increases with narrower GNR width. Because the edges of graphene serve as defects by breaking the translational symmetry of the lattice, the larger fraction of the edge in narrow GNRs will enhance the D peak [156]. The inset of Fig. 3.3a quantitatively shows the behavior by calculating the ratio of integrated D band ($I_D$) to G band ($I_G$), $I_D/I_G$, as a function of GNR width (symbols). The width

FIG. 3.2: Atomic force microscopy (AFM) images of GNR arrays. (a) $W \sim 130$ nm GNRs. (b) $W \sim 85$ nm GNRs. (c) $W \sim 65$ nm GNRs. Inset: AFM image near metal electrodes. (d) $W \sim 45$ nm GNRs. The axis units are given in microns on each panel.
dependence of the peak ratio follows a relation of $I_D/I_G = cW^{-1}$ with $c = 210$ nm (dashed line), which is consistent with previous reports of GNR characterization [95, 152]. Figure 3.3b shows the D, G, and D’ peaks in detail of fabricated GNR arrays and un-patterned graphene with 633 nm wavelength laser. Figures 3.3c-g show the Raman 2D band spectra (scattered points) for the samples. All 2D bands are fit by a single Lorentzian peak (solid red curves) with ~2650 cm$^{-1}$ peak position, which is consistent with previous reports of monolayer graphene and GNRs [152].

**FIG. 3.3:** Raman spectra of GNR arrays and un-patterned graphene. (a) Raman signal for $W \sim 130$, 85, 65, 45 nm GNRs and un-patterned graphene. Each spectrum is vertically offset for clarity. Inset is the $I_D/I_G$ ratio as a function of GNR width, consistent with the enhanced role of edge disorder in narrower GNRs [105, 152, 153]. (b) Zoomed-in D, G, and D’ bands of all samples. (c-g) 2D bands with a single Lorentzian fit for all samples, consistent with the existence of monolayer graphene.
3.2.2 Thermometry Platform and Measurements

To fabricate thermometry platform for thermal measurements, electron (e)-beam lithography was used to pattern the heater and sensor thermometers [54, 157] as long, parallel, ~200-nm-wide electrodes with current and voltage probes, with a separation of \( L \approx 260 \) nm. Electrodes were deposited by successive evaporation of SiO\(_2\) (20 nm) for electrical insulation and Ti/Au (30/20 nm) for temperature sensing. Figure 3.4 illustrates scanning electron microscopy (SEM) images of our several experimental test structures, showing graphene and GNR arrays supported

![SEM images of experimental structures](image)

**FIG. 3.4:** Measurement of heat flow in graphene ribbons. (a) Scanning electron microscopy (SEM) image of parallel heater and sensor metal lines with ~260 nm separation, on top of graphene sample (colorized for emphasis). A thin SiO\(_2\) layer under the metal lines provides electrical insulation and thermal contact with the graphene beneath. (b) Similar sample after graphene etch, serving as control measurement for heat flow through contacts and SiO\(_2\)/Si underlayers. (c) Heater and sensor lines across array of graphene nanoribbons (GNRs). (d) Magnified portion of array with GNR widths ~65 nm; inset shows atomic force microscopy (AFM) image of GNRs. Scale bars of (a-d) are 2 \( \mu \)m, 1 \( \mu \)m, 2 \( \mu \)m and 1 \( \mu \)m, respectively. (e) Three-dimensional (3D) simulation of experimental structure, showing temperature distribution with current applied through heater line.
on a SiO$_2$/Si substrate, as well as bare SiO$_2$ with graphene etched off by an oxygen plasma (however, graphene still exists under the metal electrodes, consistent with the other samples). Figure 3.5 shows the measurement set-up for the SiO$_2$ sample (Fig. 3.4b) as an example. To block environmental noise including electrostatic discharge, π-filters with a cut-off frequency of 2 MHz were inserted across all measurement lines. To control the temperature, Physical Property Measurement System (PPMS, Quantum Design) was used with a temperature range of 10 K – 363 K. Inside the PPMS, the vacuum environment is always a few $\sim 10^{-3}$ Torr, rendering convective heat losses negligible.

The measurement proceeds as follows. In the heater, we apply a sinusoidal voltage with frequency lower than 2 mHz through a standard resistor of 1 kΩ to flow current with a range of ±1.5 mA, generating a temperature gradient across the sample. To obtain the response of the

**FIG. 3.5:** Scanning electron micrograph (SEM) of thermometry platform and measurement configuration. Scale bar is 4 µm. Image taken of sample after graphene was etched off, and after all electrical and thermal measurements were completed. Dark region around “part 1” is substrate charging due to previous SEM imaging performed to obtain Fig. 3.4b in the main text.
sensor (Fig. 3.6a), we measured its resistance change by a standard lock-in method with excitation frequency 2.147 kHz and root-mean-square (rms) current 1 μA (carefully chosen to avoid additional heating). All electrical measurements were performed in a four-probe configuration. Both electrode resistances are calibrated over the full temperature range for each sample (Fig. 3.6b), allowing us to convert measured changes of resistance into changes of sensor temperature \( \Delta T_S \) as a function of heater power \( P_H \) (Fig. 3.6c). We sometimes found that the electrical resistance of the sensor slowly drifted (increased) with time at room temperature. However, this effect was stabilized after annealing the sample at 363 K for 5 min, eliminating resistance drift at room temperature. Therefore, this behavior could be related to the absorbed water on the metal electrodes.

### 3.2.3 Experimental Data and Error

Figure 3.6a shows the measured sensor resistance change, \( \Delta R_S \), as a function of the power applied to the heater, \( P_H \), at \( T = 100 \) K for the SiO$_2$ sample (Fig. 3.4b). The black (for negative heater current, \( I_H \)) and red (for positive \( I_H \)) lines overlap with each other, indicating the measurement is symmetric and reliable. The calibration for sensor and heater resistance vs. temperature is shown in Fig. 3.6b; thus, sensor heating due to heater power \( \Delta R_S \) can be converted to a temperature rise, \( \Delta T_S \), as shown in Fig. 3.6c by using the resistance-temperature calibration curve. The fitted slope of the \( \Delta T_S \) vs. \( P_H \) curve in Fig. 3.6c is 0.01797 K/μW, which is then used for the extraction of thermal properties through simulations (see Section 3.3). Figure 3.6d shows the measured ratio of \( P_H \) to \( \Delta T_S \) for all representative samples as a function of ambient temperature from 20 K to 300 K. The uncertainty of the electrical thermometry measurement is ~2% (Tables 3.1 and 3.2), which is comparable to the symbol size on this plot. Thus, although data are available down to 20 K, the values are distinguishable without ambiguity only when \( T \geq \sim70 \) K,
which is the main temperature range shown in Section 3.5.

We note that $P_H/\Delta T_S$ shown in Fig. 3.6d is not the thermal conductance through graphene, because $\Delta T_S$ is the temperature rise in the sensor, not the temperature drop from the heater to sensor, and $P_H$ is the heat generated in the heater, not the one flowing in graphene. The thermal
conductance of the graphene cannot be immediately extracted from our raw data, due to heat leakage into the substrate (a drawback of the substrate-supported thermometry method). Instead, we employ 3D simulations to carefully account for all heat flow paths and, by comparison with the experiments, to obtain the thermal conductance of the graphene samples (see Section 3.4).

Figure 3.7a shows the sensor resistance as a function of count number (time) without applying current to the heater at $T = 102$ K. The standard deviation of the scattered data points is $\delta R = 3.1$ m$\Omega$, which corresponds to $\delta T \approx 36$ mK by using calibration coefficient $0.0866 \Omega/K$ obtained in Fig. 3.6b. Thus, the error of the temperature reading is $\pm 36$ mK, primarily due to slight ambient temperature fluctuations in the PPMS (consistent with a fluctuation of $\pm 30$ mK of the displayed temperature on the PPMS monitor). Zooming into the circled region of Fig. 3.7a, we note a resistance fluctuation $\delta R = 0.17$ m$\Omega$, corresponding to a temperature uncertainty $\pm 2$ mK due to electrical measurement instruments. Therefore, during the time scales of most of our measurements our temperature accuracy is limited by the ambient temperature control of the PPMS rather than by the electrical measurements themselves.

**FIG. 3.7:** Measurement error and thermal steady-state. (a) Sensor resistance as a function of count number (time) at background $T = 102$ K. (b) Heater power, $P_H$ and corresponding resistance change in sensor, $\Delta R_S$ as a function of time.
The sweep speed of the heater power is chosen to be sufficiently slow to reach thermal steady-state between the heater and sensor. Figure 3.7b shows the heater power (\( P_H \)) sweep with time and corresponding resistance change in the sensor, \( \Delta R_S \). Data shown here correspond to the linear ramp in Fig. 3.6a. After ~15 minutes, the heater power reaches its maximum, and the change of sensor resistance follows the same trend without delay, indicating that the thermal steady-state between the heater and the sensor is established during the entire sweep process. If the sweep speed of the heater power is too fast to reach the steady-state, the data point at \( P_H \sim 110 \mu W \) in Fig. 3.6a will deviate from the linear trend. We also verified this by a comparison between the corresponding constant DC power and the above methods.

### 3.3 Model to Analyze Experimental Data

#### 3.3.1 3D Simulation to Extract Thermal Properties

To extract the thermal properties of graphene, GNRs, or the SiO\(_2\) substrate from the measured \( \Delta T_S \) vs. \( P_H \), we use a commercial software package (COMSOL) to set up a three-dimensional (3D) finite element method (FEM) model of the entire structure. A typical setup is shown in Fig. 3.8, where only a half of the sample is included due to the symmetry plane which bisects the region of interest. The size of the Si substrate is 100×50×50 \( \mu m^3 \), covered by a 290 nm thick SiO\(_2\) layer. While the simulated Si substrate is slightly smaller than the actual Si chip employed in practice (to manage computational complexity and meshing), the size of the simulated structure has been carefully chosen and verified to reproduce all heat flow through the substrate itself. Figure 3.8b shows the zoomed-in structure containing the core area of the thermometry, with GNRs, heater, and sensor highlighted by different colors. A more zoomed-in structure is shown in Fig. 3.8c, where from top to bottom different layers are 40 nm metal, 25 nm top oxide insulator, GNRs, 290 nm bottom oxide, and silicon, respectively.
To perform the simulation, the bottom surface and three side surfaces (except symmetry plane) of the Si substrate are held at the ambient temperature, i.e. isothermal boundary condition. Other outer surfaces of the whole structure are treated as insulated, i.e. adiabatic boundary condition. The Joule heating in the heater is simulated by applying a power density within the heater metal, and the stationary calculation is performed to obtain the temperature distribution in the steady state, as shown in Figs. 3.4e and 3.8d typically. After calculating the average temperature rise in the measured segment of the sensor, we obtain the simulated value of \((\Delta T_S/P_H)\). Thus, the simulation effectively fits the thermal conductance \((G)\) of the test sample between heater and thermometer. The thermal conductivity \((k = GL/A)\) of the test sample is thus an effective fitting parameter within the FEM simulator, ultimately adjusted to yield the best agreement between the

![3D Finite element method (FEM) model.](image)

**FIG. 3.8:** 3D Finite element method (FEM) model. (a) Whole structure of 3D FEM model. (b) Zoomed-in structure to show the core area of the thermometry. (c) More zoomed-in structure to show different layers. (d) Typical distribution of temperature rise due to heating in simulations which matches with measurements.
simulated and measured $\Delta T_S$ vs. $P_H$. This fitting process is implemented by using MATLAB to interface directly with the COMSOL software, taking ~0.5 hour on a single desktop computer to converge to a best-fit value at a single temperature point for a typical calculation.

Before performing a substantial amount of calculations, a series of optimizations were carried out. First, the mesh was optimized. Due to the extreme ratio of the graphene/GNRs thickness (~0.34 nm) to their typical in-plane dimensions (~10 μm), this subdomain was optimized using a swept mesh strategy rather than the typical free mesh. Other subdomains were optimized carefully using the free mesh strategy, and in the bottom oxide and Si substrate the mesh size grows gradually from the heating region to the boundaries. Second, the real substrate size is about 8×8×0.5 mm$^3$, which can be regarded as a semi-infinite substrate relative to the small heating region (~10 μm). In FEM modeling, however, we have to select a finite size for the substrate due to the computational limitation. By choosing the distance from the center of the heater to the side and bottom surfaces of the substrate as a testing variable, we found 50 μm is large enough to model this 3D heat spreading, consistent with the recent work by Jang et al. [54]. Third, the length of the six probe arms attached to the heater and sensor (see Fig. 3.8b) was chosen as 2 μm (shorter than their real counterparts), which was found to be sufficiently long to mimic any peripheral heat loss. Fourth, it was confirmed that the simulated $\Delta T_S/P_H$ is independent of the power $P_H$ applied in the heater, which means the final results do not rely on the choice of the power $P_H$.

### 3.3.2 Uncertainty Analysis

We can estimate the uncertainty of our analysis with the classical partial derivative method:

$$\frac{u_k}{k} = \sqrt{\sum_i \left( \frac{s_i u_{x_i}}{x_i} \right)^2}$$  \hspace{1cm} (3.1)
where $u_k$ is the total uncertainty in the extracted thermal conductivity $k$, $u_{x_i}$ is the uncertainty in the $i$-th input parameter $x_i$, and the dimensionless sensitivities $s_i$ are defined by

$$s_i = \frac{x_i}{k} \frac{\partial k}{\partial x_i} = \frac{\partial (\ln k)}{\partial (\ln x_i)}.$$  \hspace{1cm} (3.2)

The partial derivatives are evaluated numerically by giving small perturbation of each parameter around its typical value and redoing the extraction simulation to obtain the change of $k$. To highlight the relative importance of each input parameter, we define their absolute contributions

| Table 3.1: Uncertainty analysis for heat flow in the unpatterned “short” graphene. Example of calculated sensitivities and uncertainty analysis for the thermal conductivity of the graphene sample GS1 at 300 K. The extracted $k$ is 319 Wm$^{-1}$K$^{-1}$ and its overall uncertainty is 19%. |
| Input parameters (T = 300 K) | Units | Values $x_i$ | Uncertainty $u_{x_i}$ | $u_{x_i}/x_i$ | Sensitivity $s_i$ | Contribution $c_i = |s_i| u_{x_i}/x_i$ | $c_i^2/\Sigma c_i^2$ |
|--------------------------------|------|--------------|-------------------|-------------|-----------|----------------|----------------|
| Expt. | Sensor response | $\Delta T_s/P_H$ K/$\mu$W | 0.01635 | 0.00002 | 1.2% | 4.49 | 5.5% | 8.6% |
| Thermal | Thermal conductivity of SiO$_2$, Si, metal | $k_{ox}$ W/m/K | 1.267 | 0.04 | 3.2% | 4.25 | 13.4% | 51.6% |
| | | $k_{Si}$ | 115 | 10 | 8.7% | 0.55 | 4.8% | 6.6% |
| | | $k_{met}$ | 55 | 4 | 7.3% | 0.34 | 2.5% | 1.8% |
| | TBR of graphene/SiO$_2$, SiO$_2$/Si, metal/SiO$_2$ interfaces | $R_{gox}$ m$^2$K/W | 1.15E-08 | 2.0E-09 | 17.4% | -0.12 | 2.1% | 1.3% |
| | | $R_{oxs}$ | 9.92E-09 | 3.0E-09 | 30.2% | -0.25 | 7.6% | 16.5% |
| | | $R_{mox}$ | 1.02E-08 | 3.0E-09 | 29.5% | 0.05 | 1.5% | 0.7% |
| Geometrical | Thickness of bottom and top SiO$_2$, and metal | $t_{box}$ nm | 288 | 1 | 0.3% | -5.65 | 2.0% | 1.1% |
| | | $t_{tox}$ | 20 | 1 | 5.0% | -0.01 | 0.1% | 0.0% |
| | | $t_{met}$ | 50 | 2 | 4.0% | 0.35 | 1.4% | 0.5% |
| | Distance of H/S metal lines and H/S SiO$_2$ lines | $D_{met}$ | 494 | 5 | 1.0% | 5.38 | 5.4% | 8.5% |
| | | $D_{tox}$ | 486 | 5 | 1.0% | 2.39 | 2.5% | 1.7% |
| | Width of metal and SiO$_2$ lines | $W_{met}$ | 186 | 4 | 2.2% | -0.16 | 0.3% | 0.0% |
| | | $W_{tox}$ | 224 | 4 | 1.8% | -0.17 | 0.3% | 0.0% |
| | Half length of H/S electrodes | $L_{HS}/2$ $\mu$m | 5.86 | 0.03 | 0.5% | 0.04 | 0.0% | 0.0% |
| | Distance of 2 Voltage probes | $D_{PVV}$ | 4.23 | 0.02 | 0.5% | 3.75 | 1.8% | 0.9% |
| | Distance of Current and Voltage probes | $D_{pTV}$ | 1.04 | 0.02 | 1.9% | 0.003 | 0.0% | 0.0% |
as \( c_i = |s_i| \times (u_{x_i}/x_i) \), and relative contributions as \( c_i^2/\Sigma c_i^2 \). The uncertainty analysis for extracting \( k_{ox} \) and \( R_{oxs} \) from the SiO\(_2\) control experiment is performed in the same way.

Table 3.1 summarizes the sensitivities and uncertainty analysis for the unpatterned graphene (GS1) at 300 K. All input parameters can be separated into 3 classes: experimental data, thermal parameters, and geometric parameters. Their uncertainties are our estimates considering both random and systematic errors, and those of experimental and thermal parameters are updated appropriately as the temperature changes. The calculated sensitivities show that the graphene thermal conductivity is the most sensitive (\(|s_i| > 2\)) to the measured sensor response (\(\Delta T_S/P_H\)), thermal conductivity (\(k_{ox}\)) and thickness (\(t_{box}\)) of bottom SiO\(_2\), center-to-center distances between metal lines of heater and sensor (\(D_{met}\)), between top SiO\(_2\) lines of heater and sensor (\(D_{tox}\)), and between two voltage probes (\(D_{pVV}\)). These findings are consistent with previous work by W. Jang et al. [54] using similar substrate-supported thermometry structures. The input parameters with the greatest relative uncertainty (\(u_{x_i}/x_i\)) are all three thermal boundary resistances (TBRs), thicknesses of top SiO\(_2\) (\(t_{tox}\)) and metal (\(t_{met}\)), and the thermal conductivity of the Si substrate (\(k_{Si}\)) and metal (\(k_{met}\)). The combined effects of both sensitivities and relative uncertainties show that five largest contributions (\(c_i > \approx 5\%\)) to the overall uncertainty of our thermal measurement are from \(\Delta T_S/P_H\), \(k_{ox}\), \(k_{Si}\), \(R_{oxs}\), and \(D_{met}\). In slight contrast to Jang et al. [54], we find that uncertainties introduced by \(R_{oxs}\), \(R_{max}\) and \(t_{met}\) are non-negligible for our structure and should be considered. On the other hand, geometric parameters related to the shape and size of the graphene sheet have very small sensitivities (\(|s_i| < 0.001\)), so their contributions are negligible in uncertainty analysis and not listed in Table 3.1.
For the extraction of GNR thermal conductivity, an example of calculated sensitivities and uncertainty analysis at 300 K is summarized in Table 3.2 (here for the sample with $W \sim 65$ nm). Compared with Table 3.1, we have two more parameters: the thermal conductivity of outer graphene connected to GNRs ($k_g$) and the width of GNRs ($W_{\text{GNR}}$). The parameters with the largest sensitivities ($|s_i| > 5$) are the same as those in Table 3.1, but their values increase because

### Table 3.2: Uncertainty analysis for GNR thermal conductivity. Example of calculated sensitivities and uncertainty analysis for the thermal conductivity of GNRs with $W = 65$ nm at 300 K. The extracted $k$ is 101 Wm$^{-1}$K$^{-1}$ and its overall uncertainty is 60%.

| Input parameters (T = 300 K) | Units | Values $x_i$ | Uncertainty $u_{x_i}$ | $u_{x_i}/x_i$ | Sensitivity $s_i$ | Contribution $c_i = |s_i| \times u_{x_i}/x_i$ | $c_i^2/\Sigma c_i^2$ |
|-----------------------------|-------|--------------|-----------------------|---------------|------------------|---------------------------------|-----------------|
| Expt. Sensor response | $\Delta T_S/P_H$ | K/$\mu$W | 0.0124 | 0.0002 | 1.6% | 13.22 | 21.3% | 12.9% |
| Thermal conductivity of SiO$_2$, Si, metal, and outer graphene | $k_{\text{ox}}$ | W/m$^2$K | 1.267 | 0.04 | 3.2% | 10.38 | 32.8% | 30.5% |
| Silicon | $k_{\text{Si}}$ | | 115 | 10 | 8.7% | 2.61 | 22.7% | 14.6% |
| Metal | $k_{\text{met}}$ | | 22 | 2 | 9.1% | 0.68 | 6.2% | 1.1% |
| $k_g$ | | | 320 | 60 | 18.8% | 0.001 | 0.0% | 0.0% |
| TBR of graphene/SiO$_2$, SiO$_2$/Si, metal/SiO$_2$ interfaces | $R_{\text{ox}}$ | m$^2$K/W | 1.15E-08 | 2.0E-09 | 17.4% | -0.04 | 0.6% | 0.0% |
| | $R_{\text{oxs}}$ | | 9.92E-09 | 3.0E-09 | 30.2% | -1.00 | 30.3% | 26.1% |
| | $R_{\text{max}}$ | | 1.02E-08 | 3.0E-09 | 29.5% | 0.11 | 3.4% | 0.3% |
| Thickness of bottom and top SiO$_2$, and metal | $t_{\text{box}}$ | nm | 291 | 1 | 0.3% | -22.51 | 7.7% | 1.7% |
| | $t_{\text{ox}}$ | | 25 | 1 | 4.0% | -0.17 | 0.7% | 0.0% |
| | $t_{\text{met}}$ | | 40 | 2 | 5.0% | 0.70 | 3.5% | 0.3% |
| Distance of H/S metal lines and H/S SiO$_2$ lines | $D_{\text{met}}$ | nm | 517 | 5 | 1.0% | 14.73 | 14.2% | 5.8% |
| | $D_{\text{ox}}$ | | 509 | 5 | 1.0% | 14.25 | 14.0% | 5.6% |
| Width of metal lines, top SiO$_2$, lines, and GNRs | $W_{\text{met}}$ | nm | 218 | 4 | 1.8% | -0.64 | 1.2% | 0.0% |
| | $W_{\text{ox}}$ | | 266 | 4 | 1.5% | -2.27 | 3.4% | 0.3% |
| | $W_{\text{GNR}}$ | | 65 | 3 | 4.6% | -0.80 | 3.7% | 0.4% |
| Half length of H/S electrodes | $L_{\text{HS}/2}$ | $\mu$m | 5.77 | 0.03 | 0.5% | 0.20 | 0.1% | 0.0% |
| Distance of 2 Voltage probes | $D_{\text{PVV}}$ | $\mu$m | 4.17 | 0.02 | 0.5% | 7.80 | 3.7% | 0.4% |
| Distance of Current and Voltage probes | $D_{\text{pIV}}$ | $\mu$m | 1.04 | 0.02 | 1.9% | -0.286 | 0.5% | 0.0% |

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the total width of the GNR array is smaller than that of the unpatterned graphene. Due to the significant increase of sensitivities, the total uncertainty increases from 19% for unpatterned graphene to 60% for GNRs, while the input parameters with the greatest contributions ($c_i > 10\%$) to the total uncertainty are $\Delta T_s/P_H$, $k_{\text{ox}}$, $k_{\text{Si}}$, $R_{\text{ox}}, D_{\text{met}}$, and $D_{\text{tox}}$, the same as those for graphene along with $D_{\text{tox}}$. From the 60% total uncertainty, approximately 21% is due to measurement uncertainty and the remainder from geometric and temperature-dependent variables as listed in Table 3.2. [we note that the geometric parameters related to the shape and size of GNRs and graphene outside the heater and sensor region have very small sensitivities ($|s_i| < 0.01$) and are not listed in Table 3.2, which is also consistent with the GNR results being insensitive to $k_g$.]

For other GNR samples with different widths, the total uncertainties gradually increase from 22% to 83% at 300 K as $W$ decreases from ~130 to ~45 nm, as less heat flows in the GNR array rather than the substrate. As the temperature decreases, the uncertainties of all graphene and GNR thermal conductivities also increase due to either increased sensitivities or increased relative uncertainties of input parameters.

As mentioned earlier and shown in Tables 3.1 and 3.2, all input parameters are classified into three groups, not all of which need to be included when comparing relative GNR thermal conductivities (e.g. with width or temperature). For instance, Fig. 3.12b compares the thermal conductivities of the samples at different temperatures considering the contributions of experimental and thermal parameters to the error bars. Similarly, Fig. 3.12d compares thermal conductivities of different samples at the same temperature, considering the contributions of experimental and geometric parameters to the error bars. Different samples share the same thermal parameters and these uncertainties would only shift all $k$ values in the same direction without affecting their relative values. In the end, the differences are relatively subtle, and within the
fitting capabilities of our models, all based on the initial data above 70 K which are clearly distinguishable from one another as seen from the raw thermometry in Fig. 3.6d.

3.4 Results

Based on experimental method described above, we performed heat flow measurements from 20 to 300 K on unpatterned graphene (Fig. 3.4a), control samples with the graphene etched off (Fig. 3.4b), and arrays of GNR widths $W \approx 130, 85, 65$ and 45 nm (Figs. 3.2 and 3.4c-d). To obtain the thermal properties of our samples we used the above mentioned 3D simulations of the structures with dimensions obtained from measurements by SEM and AFM, as shown in Figs. 3.4e and 3.8. The results for the SiO$_2$ control sample, unpatterned graphene, and GNR arrays are presented in the following.

3.4.1 Thermal Properties of the SiO$_2$ Underlayer

To validate our thermometry approach, we first carefully focused on a control experiment to measure the thermal properties of the SiO$_2$ underlayer supporting our samples. The sample was first prepared as described before, including the graphene under the heater and thermometer electrodes, to reproduce the thermal contacts encountered in all samples. However, the exposed graphene was then etched by oxygen plasma, leaving the bare SiO$_2$ as shown in Figs. 3.4b and 3.5. This allows us to obtain the thermal properties of the parallel heat flow path through the contacts, supporting SiO$_2$ and substrate. Measurements were performed on part 1 and part 2 of the metal electrodes (see Fig. 3.5), and the analyzed sensor and heater temperature rises normalized by heater power as a function of the ambient temperature are shown in Fig. 3.9a.
To compare our 3D simulations to this experimental data set, we needed to fit the thermal properties of the SiO$_2$ layer (which dominate), and to a lesser degree those of the SiO$_2$-Si TBR at the bottom of the SiO$_2$ layer (which also plays a role). While the thermal conductivity of SiO$_2$ is well-known and easy to calibrate against [30, 158], to the best of our knowledge no consistent data for the TBR of the SiO$_2$-Si interface (\(R_{\text{oxs}}\)) exist as a function of temperature. Two recent studies [159, 160] suggested \(R_{\text{oxs}} \sim 5-7 \times 10^{-8} \text{ m}^2\text{KW}^{-1}\) at room temperature, but some earlier efforts [161-165] found the total TBR of metal-SiO$_2$-Si interfaces as low as \(\sim 1-3 \times 10^{-8} \text{ m}^2\text{KW}^{-1}\), putting an upper bound on \(R_{\text{oxs}}\) without being able to separate it from the total TBR. Due to this contradiction, we set out to obtain the temperature-dependent \(R_{\text{oxs}}\), treating it as another fitting parameter of our simulations in addition to the thermal conductivity of SiO$_2$ (\(k_{\text{ox}}\)). Other thermal parameters well characterized in the literature are the thermal conductivity of highly doped Si [166-168], thermal boundary resistances of the graphene-SiO$_2$ interface [44, 48] and the Au-Ti-SiO$_2$ interfaces [45]. In addition, the effective thermal conductivity of the metal electrodes (Au/Ti) was calculated from the measured electrical resistance according to the Wiedemann-Franz law.

**FIG. 3.9:** Control experiment to extract SiO$_2$ thermal properties. (a) Sensor and heater temperature rise normalized by heater power from measurements taken at part 1 and part 2 of the SiO$_2$ sample (see Fig. 3.5). (b) Extracted thermal conductivity of SiO$_2$ from two measurements compared with well-known data from Cahill [158]. The green solid line is the polynomial fit up to the 7th order to our data. (c) Extracted thermal boundary resistance of the SiO$_2$-Si interface, \(R_{\text{oxs}}\). The green solid line is the fit to our data by Eq. 3.3.
Franz Law, where an average Lorentz number \( L_z = 2.7 \times 10^{-8} \text{ W}\Omega\text{K}^{-2} \) is used for Au/Ti electrodes \[169\]. (all parameters were allowed to vary within known experimental bounds, leading to the uncertainty analysis in Section 3.3.2.)

Our extracted \( k_{ox} \) and \( R_{oxs} \) of two data sets (part 1 and 2) are shown in Figs. 3.9b and 3.9c, respectively. Our \( k_{ox} \) data are in a good agreement with well-established values reported by Cahill \[158\], and the typical uncertainty is \( \sim 5\% \) at most temperatures. By fitting our \( k_{ox} \) data with a polynomial up to the \( 7^{th} \)-order, we obtained a smooth dependence of \( k_{ox} \) on \( T \) (green solid line), and this was used to extract the thermal properties of our graphene and GNRs. Our extractions suggest \( R_{oxs} \sim 10^{-8} \text{ m}^2\text{KW}^{-1} \) at room temperature, in agreement with the reported upper bound in Refs. \[161-165\]. For the subsequent thermal analysis, our \( R_{oxs} \) data are best fit by a simple expression,

\[
R_{oxs}(T) = \frac{1.046 \times 10^{-4}}{(T + 13.4)^{2.25}} + 9.67 \times 10^{-9} \text{ m}^2\text{K/W}
\tag{3.3}
\]

as shown by the green solid line in Fig. 3.9c. Thus, this control experiment demonstrates the feasibility and reliability of our thermometry platform, also giving the first report of the temperature-dependent TBR of SiO\(_2\)-Si interfaces.

### 3.4.2 Quasi-Ballistic Thermal Transport in Short Graphene

After demonstrating the feasibility of our thermometry method by the control sample, we next examined three “short” graphene samples (GS1, 2, 3) which were not patterned into GNRs; all had length \( L \sim 260 \text{ nm} \) and width \( W \sim 12 \mu\text{m} \) between the heater and sensor thermometers (corresponding to schematic in Fig. 3.10a). Besides GS1 which is shown in Fig. 3.4a of the main paper, the SEM image of another sample (GS2) is shown in Fig. 3.11a. The third one (GS3) broke after measurements at two temperature points, which are nevertheless listed among the
Figure 3.11b displays raw data taken as ratio of heater power to sensor temperature ($P_H/\Delta T_S$) for all three samples; the corresponding data of the SiO$_2$-only sample (part 2 of Fig. 3.9a) is also plotted here for comparison. The presence of graphene notably “heats” the sensor (higher $\Delta T_S$) and is distinguishable from the SiO$_2$-only sample all the way down to ~20 K (although the GNRs become harder to distinguish below ~70 K as mentioned earlier). The extracted graphene thermal conductivities are shown in Fig. 3.11c, and the three samples show very similar values. They all decrease from ~300 Wm$^{-1}$K$^{-1}$ at 300 K to ~10 Wm$^{-1}$K$^{-1}$ at 30 K and show similar temperature dependence. The data of the “long” graphene with $L$ ~10 μm from Seol et al. [49] are also plotted in Fig. 3.11c (black dots).
we compare the sample thermal conductance to the theoretical ballistic limits in Fig. 3.11. Recalling the relationship between conductance and conductivity, \( G = kA/L \), where \( A \) is the cross-sectional area of heat flow, \( A = WH \), with \( W \) and \( H = 0.335 \text{ nm} \) as the width and thickness of the graphene samples, respectively. The theoretical ballistic conductance per unit cross-sectional area \( G_{\text{ball}}/A \) of graphene (solid line in Fig. 3.11d) is calculated by using the full phonon dispersion of graphene and integrating over the entire 2D Brillouin zone (see Sections 5.4.1 and 5.3.2). For convenience, we note that the \( G_{\text{ball}}/A \) of graphene can be approximated analytically as.
\( G_{\text{ball}}/A \approx \left[ 1/(4.4 \times 10^5 \ T^{1.68}) + 1/(1.2 \times 10^{10}) \right]^{-1} \ \text{WK}^{-1}\text{m}^{-2} \) over the temperature range 1-1000 K, as a fit to full numerical calculations. As shown in Fig. 3.11d, our three “short” graphene samples all display on average \( \sim 35\% \) of the ballistic conductance limit, indicating they reach a quasi-ballistic conduction regime (schematic in Fig. 3.10b). The data for the 10-\( \mu \text{m} \) “long” sample from Seol et al. [49] show \( <2\% \) of ballistic limit on average, indicating a diffusive transport regime (schematic in Fig. 3.10a) as would be expected for a sample much longer than the phonon MFP \( (W, L \gg \lambda) \). Both percentages are consistent with a simple estimation of transmission probability \( \sim L_{\text{bs}}/(\lambda_{\text{bs}} + L) \) using their own lengths and back scattering mean free path \( \lambda_{\text{bs}} = (\pi/2)\lambda \sim 160 \text{ nm} \) (see Section 3.4.3) where the intrinsic phonon MFP \( \lambda \sim 100 \text{ nm} \) for most temperatures.

### 3.4.3 Length dependence of thermal conductivity

To understand different transport behaviors in short and long graphene, we recall that in the ballistic limit \( (L \ll \lambda) \) the conductance rather than the conductivity approaches a constant at a given temperature [29, 112, 170], \( G_{\text{ball}}(T) \). Nevertheless, the thermal conductivity is the parameter typically used for calculating heat transport in practice, and for comparing different materials and systems. Thus, the well-known relationship \( k = (G/A)L \) imposes the conductivity \( k \) to become a function of length in the ballistic regime and to decrease as \( L \) is reduced. This situation becomes evident when we plot the thermal conductivity in Figs. 3.11c and 3.12b, finding \( k \approx 320 \ \text{Wm}^{-1}\text{K}^{-1} \) for our “short” and wide samples at room temperature (schematic Fig. 3.10b), almost a factor of two lower than the large graphene [49] (schematic Fig. 3.10a). We note that both unpatterned samples here and in Ref. [49] were supported by SiO\(_2\), showed no discernible defects in the Raman spectra, and the measurements were repeated over three samples (Fig. 3.11) with similar results obtained each time.
The transition of thermal conductivity from diffusive to ballistic can be captured through

FIG. 3.12: Thermal conduction scaling in GNRs. (a) Thermal conductance per cross-sectional area ($G/A$) vs. temperature for our GNRs ($L \approx 260$ nm, $W$ as listed, see Fig. 3.10c), a “short” unpatterned sample ($L \approx 260$ nm, $W \approx 12$ μm, see Fig. 3.10b), and a “large” sample from Seol et al. [49] ($L \approx 10$ μm, $W \approx 2.4$ μm, see Fig. 3.10a). The short but wide graphene sample attains up to ~35% of the theoretical ballistic heat flow limit [29, 112, 170]. (b) Thermal conductivity for the same samples as in (a) (also see Fig. 3.14a). (c) Thermal conductivity reduction with length for “wide” samples ($W \gg \lambda$), compared to the ballistic limit ($k_{\text{ball}} = G_{\text{ball}}L/A$) at several temperatures. Symbols are data for our “short” unpatterned graphene samples (Figs. 3.4a and 3.10b), and “large” samples from Seol et al. [49] (Fig. 3.10a). Solid lines are model from Eq. 3.4. (d) Thermal conductivity reduction with width for GNRs, all with $L \approx 260$ nm (Figs. 3.4c-d and 3.10c). Solid lines are experimental data from (b), open symbols are interpolations for the listed temperature; lines are fitted model from Eq. 3.5. The thermal conductivity of plasma-etched GNRs in this work appears lower than that estimated for GNRs from unzipped nanotubes [144] at a given width, consistent with a stronger effect of edge disorder [153]. Also see Fig. 3.13a.

The transition of thermal conductivity from diffusive to ballistic can be captured through
simple models [171], similar to the apparent mobility reduction during quasi-ballistic charge transport observed in short-channel transistors [172, 173]:

\[
k(L) = \sum_b \left( \frac{A}{LG^b_{ball}} + \frac{1}{k^b_{diff}} \right)^{-1} \approx \frac{G_{ball}}{A} \left[ \frac{1}{L} + \frac{1}{(\pi/2)\lambda} \right]^{-1}.
\] (3.4)

The first equality is a “three-color” model with \( b \) the phonon branch (longitudinal acoustic, LA; transverse, TA; flexural, ZA), \( G^b_{ball} \) calculated using the appropriate dispersion [29], and \( \sum k^b_{diff} = k_{diff} \) the diffusive thermal conductivity. At \( T = 300 \) K, \( k_{diff} \approx 560 \pm 50 \text{ Wm}^{-1}\text{K}^{-1} \), and \( k^b_{diff} = 148, 214, 198 \text{ Wm}^{-1}\text{K}^{-1} \) for \( b = ZA, TA, LA \) modes, respectively [49]. A simpler “gray” approximation can also be obtained by dropping the \( b \) index, \( k(L) \approx \frac{G_{ball}/A}{(L^2 \lambda) \approx 4.2 \times 10^9 \text{ WK}^{-1}\text{m}^2} \) at room temperature [96] (see Section 3.4.2). The second expression in Eq. 3.4 is a Landauer-like model [171, 174], with \( \pi/2 \) accounting for angle averaging [175] in 2D to obtain the phonon backscattering MFP.

We compare the simple models in Eq. 3.4 with the experiments in Fig. 3.12c and find good agreement over a wide temperature range. The Eq. 3.4 also yields our first estimate of the intrinsic phonon MFP in SiO\(_2\)-supported graphene, \( \lambda \approx (2/\pi)k_{diff}/(G_{ball}/A) \approx 90 \) nm at 300 K and 115 nm at 150 K. (The same argument estimates an intrinsic phonon MFP \( \lambda \approx 300-600 \) nm in freely suspended graphene at 300 K, if a thermal conductivity 2000-4000 Wm\(^{-1}\)K\(^{-1}\) is used [21, 23, 24, 58].) This phonon MFP is the key length scale which determines when the thermal conductivity of a sample becomes a function of its dimensions, in other words when \( L \) and \( W \) are comparable to \( \lambda \). Based on Fig. 3.12c, we note that ballistic heat flow effects should become non-negligible in all SiO\(_2\)-supported graphene devices shorter than approximately 1 \( \mu \)m.

3.4.4 Width dependence of thermal conductivity

Figure 3.12a also displays in-plane thermal conductance per area \( (G/A) \) for our measured
GNRs ($L \approx 260$ nm, $W \approx 130, 85, 65$ and $45$ nm). As the width decreases, thermal conduction returns from quasi-ballistic to diffusive regimes gradually (corresponding to schematic Fig. 3.10c). In parallel, Fig. 3.10 summarizes schematics of the size effects and all three transport regimes discussed, corresponding to the samples measured in Fig. 3.12.

We now turn to the width-dependence of heat flow in narrow GNRs. Our experimental data in Figs. 3.12b and 3.12d show a clear decrease of thermal conductivity as the width $W$ is reduced to a regime comparable to the intrinsic phonon MFP. For instance, at room temperature $k \approx 230, 170, 100$, and $80$ Wm$^{-1}$K$^{-1}$ for GNRs of $W \approx 130, 85, 65$ and $45$ nm, respectively, and same $L \approx 260$ nm. To understand this trend, we consider $k$ limited by phonon scattering with edge disorder [176, 177] through a simple empirical model with a functional form suggested by previous work on rough nanowires [178, 179] and GNR mobility [180]:

$$k_{eff}(W, L) \approx \left[ \frac{1}{c} \left( \frac{\Delta}{W} \right)^n + \frac{1}{k(L)} \right]^{-1}. \quad (3.5)$$

Here $\Delta$ is the rms edge roughness and $k(L)$ is given by Eq. 3.4 [$k(L) = 346, 222, 158, 37$ Wm$^{-1}$K$^{-1}$ for $T = 300, 190, 150, 70$ K, respectively]. The solid lines in Fig. 3.12d show good agreement with our GNR data ($L \approx 260$ nm) using $\Delta = 0.6$ nm and a best-fit exponent $n = 1.8 \pm 0.3$, as well as $c$ fitted to be 0.04019, 0.02263, 0.01689, and 0.00947 Wm$^{-1}$K$^{-1}$ for $T = 300, 190, 150$, and 70 K, respectively. Note that we cannot assign overly great physical meaning to the parameter $c$ because the empirical model can only fit $\Delta^n/c$, not $\Delta$ or $c$ independently. The simple model appears to be a good approximation in a regime with $\Delta \ll W$, where the data presented here were fitted. However it is likely that this simple functional dependence would change in a situation with extreme edge roughness [81], where the roughness correlation length (which cannot be directly quantified here) could also play an important role.
Nevertheless, the nearly \( W \)-squared dependence of thermal conductivity in narrow GNRs with edge roughness is consistent with previous findings for rough nanowires \([178, 179]\), and also similar to that suggested by theoretical studies of GNR electron mobility \([180]\). The precise scaling with \( \Delta \) is ostensibly more complex \([176, 177]\) than can be captured in a simple model, as it depends on details of the phonon dispersion, the phonon wave vector, and indirectly on temperature. However the \( \Delta \) estimated from the simple model presented above is similar to that from extensive numerical simulations below, and to that measured by transmission electron microscopy (TEM) on GNRs prepared under similar conditions \([153]\). Thus, the simple expressions given above can be taken as a practical model for heat flow in substrate-supported GNRs with edge roughness \( (\Delta \ll W) \) over a wide range of dimensions, corresponding to all size regimes in Fig. 3.10.

It is instructive to examine some similarities and differences between our findings here vs. previous results regarding size effects on charge carrier mobility in GNRs with dimensions comparable to the phonon or electron MFP. Figure 3.13 displays the width \( W \) dependence of our GNR thermal conductivity side-by-side with the electrical mobility measured by Yang and Murali \([147]\) on similar samples (Fig. 3.13a is re-plot of Fig. 3.12d, here using log axis). Both the GNR thermal conductivity and electrical mobility show a similar trend with \( W \), starting to decrease significantly when scattering becomes edge limited. However it is apparent that their fall-off occurs at different critical widths: \( W \approx 200 \) nm for thermal conductivity and \( W \approx 40 \) nm for electrical mobility. Above these widths, the thermal conductivity is limited by phonon-substrate scattering, while the electrical mobility is limited by electron scattering with substrate impurities. The difference between their critical \( W \) is consistent with the intrinsic phonon MFP \( \lambda_{ph} \approx 100 \) nm being approximately five times larger than the intrinsic electron MFP \([104]\) \( \lambda_{el} \approx 20 \)
nm in SiO$_2$-supported graphene. (We note phonons are entirely responsible for the thermal conductivity of these GNRs, with a negligible electronic contribution [144]). Thus, the fall-off of thermal conductivity and electrical mobility corresponds approximately to GNR widths approximately twice the phonon and electron MFPs. Interestingly, this also suggests a GNR width regime ($\sim 40 < W < \sim 200$ nm) where the thermal conductivity is reduced from intrinsic values but the electrical mobility is not yet affected by edge disorder. This suggests the possibility of manipulating heat and charge flow independently in such narrow edge-limited structures. Further control of such behavior could also be achieved if substrates with different roughness, impurity density, and vibrational (phonon) properties are used.

### 3.5 Discussion and BTE Calculations

#### 3.5.1 Low-$T$ Scaling and Comparison with CNT
Figure 3.14a shows the extracted thermal conductivity of our “short” graphene (GS1) and GNRs for the full temperature range measured, down to ~20 K (however, we recall that GNR measurements are challenging to distinguish below ~70 K, as previously mentioned). We can fit the thermal conductivity as \( k = \alpha T^\beta \) below ~200 K, and the obtained power \( \beta \) is shown as an inset of Fig. 3.14a. We find that \( \beta \) decreases from ~1.6 for the unpatterned graphene to ~1 for narrow GNRs. However, we note that this does not necessarily mark a transition to one-dimensional (1-D) phonon flow, as the GNRs here are much wider than the phonon wavelengths (few nm).

Thus, the simple model is given as a convenient analytic estimate, and the exponent \( \beta \) represents the complex physical behavior of GNR heat flow due to the increasing heat capacity (which scales as \( ~T^{1.5} \)) and the slightly decreasing phonon MFP in this \( T \) range.

We also compare our extracted graphene and GNR thermal conductance with carbon nanotubes (CNTs) in Fig. 3.14b. We perform this comparison with the calculated ballistic upper limit, with a single-wall carbon nanotube (SWCNT) by M. Pettes et al. [75], and with multi-wall

![Graph showing thermal conductivity and G/A values for different types of graphene and GNRs](image)

**FIG. 3.14:** Complete data sets including low-\( T \) range and comparison with CNTs. (a) Extracted thermal conductivity of graphene (GS1) and GNRs, same as Fig. 3.12b but with low-\( T \) (20–60 K) data included for completeness. Long graphene data are from Seol et al. [49]. Inset: power exponent \( \beta \) vs. GNR width fit from \( k = \alpha T^\beta \) (see text). (b) Thermal conductance (\( G/A \)) of our data compared with those of long graphene [49], ballistic limit, SWCNT of M. Pettes et al. [75], and MWCNTs from studies of P. Kim et al. [71], M. Pettes et al. [75], and M. Fujii et al. [181].
carbon nanotubes (MWCNTs) by P. Kim et al. [71], M. Pettes et al. [75], and M. Fujii et al. [181]. We find that our short graphene data (red filled dots) and P. Kim’s MWCNT data [71] (open black squares) have the highest values, both reaching up to ~35% of the ballistic limit of graphene.

3.5.2 Effects of Contacts

We note that the 3D simulations automatically include all known contact resistance effects, including those of the graphene-SiO₂ and SiO₂-metal interfaces, matched against data from the literature and our control experiments (see Section 3.4.1). To provide some simple estimates, the contact thermal resistance (per electrode width) is $R_C \approx 0.7 \text{ m·KW}^{-1}$, the “wide” unpatterned graphene thermal resistance is $R_G \approx 2.5 \text{ m·KW}^{-1}$, and that of the GNR arrays is in the range $R_{\text{GNR}} \approx 4$ to 32 m·KW⁻¹ (from widest to narrowest). The graphene is not patterned under the electrodes, thus the contact resistance remains the same for all samples. The 3D simulations also account for heat spreading through the underlying SiO₂, and our error bars include various uncertainties in all parameters (see Section 3.3.2).

We also consider the effects of measurement contacts and how they relate to the interpretation of sample length in the quasi-ballistic heat flow regime. As in studies of quasi-ballistic electrical transport [172, 173], we defined the “channel length” $L$ as the inside edge-to-edge distance between the heater and thermometer electrodes (Fig. 3.10c). Simple ballistic theory assumes contacts with an infinite number of modes, and instant thermalization of phonons at the edges of the contacts. The former is well approximated here by electrodes two hundred times thicker than the graphene sheet, however phonons may travel some distance below the contacts before equilibrating. The classical, continuum analog of this aspect is represented by the thermal transfer length ($L_T$) of heat flow from the graphene into the contacts [129], which is automatica-
ly accounted in our 3D simulations (Fig. 3.4e). However, a sub-continuum perspective [182] reveals that phonons only thermally equilibrate after traveling one MFP into the graphene under the contacts. Previous measurements of oxide-encased graphene [54] had estimated a thermal conductivity $k_{\text{enc}} = 50$-$100$ Wm$^{-1}$K$^{-1}$, which suggests a phonon MFP $\lambda_{\text{enc}} = (2k_{\text{enc}}/\pi)/(G_{\text{ball}}/A) \approx 8$-$15$ nm under the contacts. This adds at most 12% to our assumption of edge-to-edge sample length (here $L \approx 260$ nm), a small uncertainty which is comparable to the sample-to-sample variation from fabrication, and to the size of the symbols in Fig. 3.12c. (The relatively low thermal conductivity of encased monolayer graphene [54] is due to scattering with the SiO$_2$ sandwich, although some graphene damage from the SiO$_2$ evaporation [183] on top is also possible.)

### 3.5.3 BTE Calculations

To gain deeper insight into our experimental results, we employ a numerical solution of the Boltzmann transport equation (BTE) with a complete phonon dispersion [177, 184]. Our approach is similar to previous work [28, 49, 184], but accounting for quasi-ballistic phonon propagation and edge disorder scattering in short and narrow GNRs, respectively. We obtain the thermal conductivity by solving the Boltzmann transport equation in the relaxation time approximation including scattering at the rough GNR edges [177]. The simulation uses the phonon dispersion of an isolated graphene sheet, which is a good approximation for SiO$_2$-supported graphene within the phonon frequencies that contribute most to transport [101], and at typical graphene-SiO$_2$ interaction strengths [97]. (However, we note that artificially increasing the graphene-SiO$_2$ coupling, e.g. by applying pressure [185], could lead to modifications of the phonon dispersion and hybridized graphene-SiO$_2$ modes [97].) We assume a graphene monolayer thickness $H = 0.335$ nm, and a concentration of 1% $^{13}$C isotope point defects [21, 49]. The
FIG. 3.15: Computed phonon scattering rates at $T = 300$ K for a GNR with $W = 65$ nm, $L = 260$ nm, and $\Delta = 0.65$ nm. Substrate contact patch radius is $a = 8.75$ nm. Rates are plotted as a function of energy for each scattering mechanism and their total; however, each dot represents one phonon mode. Note that angle-dependent mechanisms like contact and edge roughness scattering have additional dependence on the angle of the phonon velocity vector, which can lead to different rates for the same value of phonon energy.
interaction with the substrate is modeled through perturbations to the scattering Hamiltonian [49] at small patches where the graphene is in contact with the SiO₂, with nominal patch radius \( a = 8.75 \text{ nm} \). Anharmonic three-phonon interactions of both normal and umklapp type are included in the relaxation time. An equivalent 2D ballistic scattering rate \([171, 175]\) ~\( 2v_x/L \) is used in the numerical solution (\( x \) is direction along graphene) to account for transport in short GNRs.

Figure 3.16a finds good agreement of thermal conductivity between our measurements and the BTE model across all samples and temperatures. We obtained the best fit for GNRs of width 130 and 85 nm with rms edge roughness \( \Delta = 0.25 \) and 0.3 nm, where the gray bands in Fig. 3.16a correspond to \( \pm 5\% \) variation around these values. For GNRs of widths 65 and 45 nm the gray bands correspond to edge roughness ranges \( \Delta = 0.35-0.5 \) and 0.5-1 nm, respectively. We note that, unlike the empirical model of Eq. 3.5, the best-fit BTE simulations do not use a unique value of edge roughness \( \Delta \). This could indicate some natural sample-to-sample variation in edge roughness from the fabrication conditions, but it could also be due to certain edge scattering physics (such as edge roughness correlation [81] and phonon localization [186]) which are not yet captured by the BTE model.

Figure 3.16b examines the scaling of MFPs by phonon mode, finding they are strongly reduced as the GNR width decreases below \( \sim 200 \text{ nm} \), similar to the thermal conductivity in Fig. 3.12d. The frequency-dependent phonon MFP is directly obtained from the calculated total scattering rate (e.g. Fig. 3.15f). The MFP for each phonon mode is calculated as an average over the entire frequency spectrum, weighted by the frequency-dependent heat capacity \( c^b(\omega) \) and group velocity \( v^b(\omega) \),

\[
\langle \lambda^b \rangle = \frac{\int c^b(\omega)v^b(\omega)\lambda^b(\omega)d\omega}{\int c^b(\omega)v^b(\omega)d\omega}.
\]  

(3.6)
We note that LA and TA modes, which have larger intrinsic MFPs, are more strongly affected by GNR edge disorder. On the other hand ZA modes are predominantly limited by substrate scattering and consequently suffer less from edge disorder, consistently with recent findings from...
molecular dynamics (MD) simulations [97, 101].

Increasing edge disorder reduces phonon MFPs (Fig. 3.17d), and the thermal conductivity is expected to scale as shown in Fig. 3.16c. In the BTE model the edge roughness scattering is captured using a momentum-dependent specularity parameter,

\[ p(q) = \exp\left( -4q^2 \Delta^2 \sin^2 \theta_E \right), \]

(3.7)

where \( q \) is the magnitude of the phonon momentum and \( \theta_E \) is the angle between the direction of phonon momentum and the edge. This specular parameter indicates that small wavelength (large \( q \)) phonons are more strongly affected by line edge roughness. However, as \( \Delta \) increases the specularity parameter saturates, marking a transition to fully diffuse edge scattering, and also to a regime where substrate scattering begins to dominate long wavelength phonons in substrate-supported samples. This transition cannot be captured by the simplified \( \Delta^n \) dependence in the empirical model of Eq. 3.5.

To further illustrate such distinctions, Fig. 3.16d displays the energy (frequency \( \omega \)) dependence of phonon MFPs for a “small” GNR and a “large” SiO\(_2\)-supported graphene sample (corresponding to Figs. 3.10c and 3.10a, respectively). Low-frequency substrate scattering (proportional to \( \sim 1/\omega^2 \)) dominates the large sample [49, 97], while scattering with edge disorder affects phonons with wavelengths comparable to, or smaller than, the roughness \( \Delta \). Therefore, larger \( \Delta \) can affect more long-wavelength (low energy) phonons, but only up to \( \Delta \sim 1 \) nm, where the effect of the substrate begins to dominate in the long wavelength region. (Also seen in Fig. 3.16c.) Such a separation of frequency ranges affected by substrate and edge scattering could provide an interesting opportunity to tune both the total value and the spectral components of thermal transport in GNRs, by controlling the substrate and edge roughness independently.
We also show that the lattice thermal conductivity (Fig. 3.17a) and the phonon MFP (Fig. 3.17b) both scale with the length of the GNR in “short” ribbons due to the MFP being limited to about half the length ($\tau_{\text{ball}} = \frac{1}{2}L/|v^{\text{b}}(q)|$). A difference exists between wide ($W = 2 \, \mu m$) and narrow
\( W = 65 \text{ nm} \) ribbons due to the presence of edge roughness scattering in the narrow ribbons. In the wide ribbons, the most significant scattering mechanism is substrate scattering, which limits the phonon MFP to around 100 nm (the value to which the total MFP converges for “long” ribbons in Fig. 3.17b). We note that this value is very nicely consistent with the average substrate-limited (or intrinsic) MFP deduced through a simple comparison with the ballistic conductance limits in the main text (Fig. 3.12 and surrounding discussion).

For a sample length \( L \sim 200 \text{ nm} \), or approximately twice the intrinsic MFP, the length-dependent ballistic scattering rate is comparable to the substrate scattering rate and the effective thermal conductivity and phonon MFP become one-half of the substrate-limited values (Fig. 3.17a-b for “wide” sample). However, in narrow GNRs, the diffuse scattering at the edges limits the phonon MFP to approximately one-half of the width \( W \) (the edge-roughness-limited MFP also depends on the rms edge roughness, as shown in Fig. 3.17d). Consequently, thermal transport in narrow GNRs is mostly diffusive until the length is reduced to values comparable to the width, and the transport again becomes quasi-ballistic (shown by solid lines in Fig. 3.17a-b).

**3.6 Summary**

In conclusion, we investigated heat flow in SiO\(_2\)-supported graphene samples of dimensions comparable to the phonon MFP. Short devices \(( L \sim \lambda \), corresponding to Fig. 3.10b schematic\) have thermal conductance much higher than previously found in micron-sized samples, reaching 35% of the ballistic limit at 200 K and 30% (~1.2 GWK\(^{-1}\)m\(^{-2}\)) at room temperature. However, narrow ribbons \(( W \sim \lambda \), corresponding to Fig. 3.10c schematic\) show decreased thermal conductivity due to phonon scattering with edge disorder. Thus, the usual meaning of thermal conductivity must be carefully interpreted when it becomes a function of sample dimensions. The results also suggest powerful means to tune heat flow in 2D nanostructures through the
effects of sample width, length, substrate interaction and edge disorder.
CHAPTER 4

SUBSTRATE-SUPPORTED THERMOMETRY PLATFORM FOR NANO-MATERIALS LIKE GRAPHENE, NANOTUBES, AND NANOWIRES*

4.1 Introduction

To probe nanoscale thermal conduction, different measurement techniques have been developed, such as the $3\omega$ method, scanning thermal microscopy, time-domain thermoreflectance, and various bridge platforms [30]. Among them, using a microfabricated suspended bridge can directly measure in-plane heat flow through nanostructures by electrical resistance thermometry [69, 187-189]. This suspended thermometry has good measurement accuracy and has been widely used for nanofilms [189-191], one-dimensional (1D) materials like nanowires (NWs) [187, 188] and nanotubes [73, 76], as well as two-dimensional (2D) materials like hexagonal boron nitride [192] and graphene [51, 52]. A major drawback of this platform is that the fabrication is complicated and the test sample has to be either fully suspended [51, 69, 73, 76, 187-192] or supported by a suspended dielectric (e.g. SiNx) membrane [52, 78]. This limits the diversity of measurable materials and makes the suspended platform fragile.

To overcome these limitations, substrate-supported platforms could be preferred and have been recently employed in thermal studies of Al nanowires [157], encased graphene [54] and graphene nanoribbons in our previous work [55]. Nanomaterials are almost always substrate-supported in nanoscale electronics [193], thus a substrate-supported platform has the advantage of testing devices including extrinsic substrate effects [1, 106], which could be different from their intrinsic thermal properties (probed by suspended platforms) [21, 23, 24]. Substrate-

supported thermometry platforms could also readily be incorporated in industrial mask designs and fabrication processes as thermal test structures in addition to existing electrical test structures. Thus, measuring the thermal conduction of nanomaterials on a substrate is crucial from a practical viewpoint.

In this work, we critically examine the applicability and limitations of nanoscale thermal measurements based on a substrate-supported platform utilizing electrical resistance thermometry. As a prototype, the thermal conductivity of graphene on a SiO$_2$/Si substrate was experimentally tested. The fabrication of this supported platform is much easier than that of suspended platforms, but as a trade-off the thermal conductivity extraction is slightly more challenging and must employ a three-dimensional (3D) heat conduction simulation of the test structure. Through careful uncertainty analysis, we find that the supported platform can be optimized to improve the measurement accuracy. The smallest thermal sheet conductance that can be measured by this method within a 50% error is $\sim$25 nWK$^{-1}$ at room temperature, which means the supported platform can be applied to nanomaterials like carbon nanotube (CNT) networks, nanotube or nanowire arrays, and even a single Si nanowire. Additionally, it is suitable for materials which cannot be easily suspended, like many polymers, and the substrate is not limited to SiO$_2$/Si but can be extended to other substrates such as flexible plastics.

4.2 Thermometry Platform Demonstration

4.2.1 Platform Structure and Measurement

Figure 4.1a shows a scanning electron microscopy (SEM) image of a typical supported thermometry platform, here applied to a monolayer graphene sample. (In general, the sample to be measured is prepared on a SiO$_2$/Si substrate, though this is not always necessary, as we will show below.) Then, two parallel, long metal lines with at least four probe arms are patterned by
electron-beam (e-beam) lithography as heater and sensor thermometers. If the sample is conductive (here, graphene), then the heater and sensor must be electrically insulated by a thin SiO$_2$ layer, as seen in the Fig. 4.1b cross-section. To perform measurements, a DC current is passed through one metal line (heater) to set up a temperature gradient across the sample, and the electrical resistance changes of both metal lines (heater and sensor) due to the heating are monitored. After temperature calibration of both metal line resistances the measured changes in resistance ($\Delta R$) can be converted into changes in temperature of the heater and sensor, $\Delta T_H$ and $\Delta T_S$, as a function of heater power $P_H$.

**FIG. 4.1:** (a) Scanning electron microscopy image of supported thermometry platform designed to measure thermal conductivity of a graphene sample (purple) on a SiO$_2$/Si substrate. (b, c) 2D and 3D finite element models used to simulate heat conduction in the supported thermometry platform, respectively. In the 2D model, only the cross-section is included and the zoom-in shows the typical temperature distribution with heating current applied through the heater. (d) Zoomed-in temperature distribution around heater and sensor obtained from 3D simulation, which matches with measured temperature. The white dashed lines indicate the outline of the sample, which is highlighted by the red line and rectangle in (b) and (c), respectively. The detailed shape and size of the sample will not affect the simulation.
As the sample is not suspended, a control experiment should be performed after removing the exposed parts of the sample and repeating the above measurements to independently find the thermal properties of the heat flow path through the contacts and substrate. Etching away the sample is important, rather than simply performing the measurement without the original sample, because it preserves the sample portion beneath the heater and sensor electrodes, i.e. the same contact resistance in both configurations. Using this approach, in previous work [55] we obtained the thermal conductivity of the underlying SiO$_2$ within 5% error of widely known values, which also helps support the validity of this approach.

4.2.2 Model to Extract Thermal Conductivity

We note that the fabrication of the supported platform can be performed with greater yield than that of suspended platforms, but the thermal conductance between the heater and sensor cannot be obtained analytically as in the suspended case, due to non-negligible heat leakage into the substrate. Therefore, numerical modeling of such heat conduction must be employed to extract the thermal conductivity of the sample. For comparison, we considered both 2D and 3D finite element models of the sample, which are implemented by a commercial software package (COMSOL). In the 2D model, only the cross-section of the platform is simulated, and the Si substrate size is chosen as $2L_S \times L_S$ (Fig. 4.1b). In the 3D model, half of the platform needs to be simulated due to the symmetry plane which bisects the region of interest, and the Si substrate size is chosen as $2L_S \times L_S \times L_S$ (Fig. 4.1c). To perform the simulation, in both 2D and 3D models the bottom and side boundaries (except symmetry plane in 3D) of the Si substrate are held at the ambient temperature, i.e. isothermal boundary condition. Other outer boundaries of the whole structure are treated as insulated, i.e. adiabatic boundary condition. Joule heating is simulated by applying a power density within the heater metal, and the calculation is performed to obtain the
temperature distribution in steady state, as shown in Figs. 4.1b and 4.1d for the 2D and 3D models, respectively. After calculating the average temperature rises in the measured segments of the heater and sensor, we obtain the simulated values of $\Delta T_H$ and $\Delta T_S$ vs. $P_H$. Then, we can match these with the measured values by fitting the thermal conductance $G$ of the test sample between the heater and sensor. The thermal conductivity of the sample, $k = GL/A$, can then be extracted. Here $L$ is the sample length, i.e. the heater-sensor separation and $A$ is the cross-sectional area, i.e. the sample width $W$ times thickness $h$ (see Figs. 4.1b and 4.1d).

To correctly obtain the sample thermal conductivity, the simulated size $L_S$ of the Si substrate must be carefully chosen because the real Si chip is $\sim 0.5$ mm thick and several mm wide. The chip dimensions are semi-infinite compared to the small heating region ($\sim 10$ μm) and cannot be fully included due to computational grid limits. Thus, the simulated $L_S$ should be large enough to model the heat spreading and give a converged value of the extracted $k$. For the 2D and 3D models, the extracted thermal conductivities as a function of simulated $L_S$ from our graphene measurement [55] at 270 K are shown in Fig. 4.2a. Here, for the 3D model, we further considered two cases: heater and sensor with probe arms (as shown in Fig. 4.1d), and without probe...
arms (as shown in Fig. 4.3a), because the latter has a more direct correspondence to the 2D model (reflected by the similar extracted $k$ for small $L_S$). Comparing these two cases also allows us to test how many details of the electrode geometry should be included.

It is clear that the extracted $k$ by the 2D model continues decreasing as the simulated $L_S$ increases, whereas the two 3D models give converged $k$ when the simulated $L_S$ is sufficiently large ($\geq 50 \, \mu m$). The 2D model is insufficient because it neglects the heat spreading along the $y$-direction perpendicular to the 2D plane. Although the heater and sensor length ($\sim 10 \, \mu m$ or similar to the sample width) are long compared to their separation $L_{HS}$ ($\sim 0.5 \, \mu m$), we find that 3D heat spreading about 10 $\mu m$ away from the heating center cannot be neglected (see Fig. 4.3b). As the simulated $L_S$ increases, the effect of neglecting the heat spreading along the $y$-direction becomes stronger in the 2D model. Thus, we find that the 3D simulation is preferable in order to fully capture all heat spreading effects due to the finite size of the sample.

**FIG. 4.3:** (a) Structure and temperature distribution for the 3D model without probe arms, which can be regarded as the one extruded from the 2D model, and hence has a better correspondence to the 2D model than the 3D with probe model. (b) Evolution of temperature isosurface shape in 3D simulation. When heat spreads out from the heater, the isosurface is close to a cylinder at the beginning (inset), behaving as 2D heat conduction, while it changes to a sphere after $\sim 10 \, \mu m$ from the center, indicating heat spreading along the third direction cannot be ignored, which is the reason why the 2D model fails.
Figure 4.2a also shows that simulating the effect of heat loss through the voltage probe arms is necessary. As shown in Fig. 4.2b, if the same k of the sample is used, the simulated temperature rise along the sensor for the “3D with probe” case (solid red line) is lower than that for the “3D without probe” case (solid black line), and in the former case there are temperature dips at the points where the probe arms are connected due to heat leakage through them. Figure 4.2c shows that the extracted k increases and saturates gradually as the simulated length of the probe arms $L_{probe}$ increases, indicating $L_{probe} \geq 1.5 \, \mu m$ is sufficiently long to catch its effect and this converged value finally provides a correct k of the sample.

4.3 Uncertainty Analysis and Optimization

4.3.1 Uncertainty Analysis of Measurements

Next, we turn to the estimation of uncertainty in the extracted thermal conductivity k, which can be accomplished by the classical partial derivative method: $u_k/k = \left( \sum_i (s_i \times u_{x_i}/x_i)^2 \right)^{1/2}$, where $u_k$ is the total uncertainty of extracted thermal conductivity k, $u_{x_i}$ is the estimated uncertainty for each input parameter $x_i$ of the simulation, and the sensitivity $s_i$ is defined by $s_i = (x_i/k) \partial k/\partial x_i = \partial (\ln k)/\partial (\ln x_i)$. The sensitivity is evaluated numerically by giving a small perturbation for each input parameter around its typical value and redoing the extraction simulation to obtain the change of k [54]. To highlight the relative importance of each input parameter, we define its absolute contribution as $c_i = |s_i|x(u_{x_i}/x_i)$, and a relative contribution as $c_i^2/\Sigma c_i^2$. As an example, the calculated sensitivities and uncertainty analysis for the extracted k in Fig. 4.2c are shown in Table 4.1. The total uncertainty in this case is ~20.8%, and it mainly arises from the contributions ($c_1 > 5\%$) of the thermal conductivity of bottom SiO₂ ($k_{ox}$), thermal boundary resistance (TBR) of the SiO₂/Si interface ($R_{oxs}$), measured sensor response ($\Delta T_s/P_H$), thermal conductivity of Si substrate ($k_{Si}$), and heater-sensor midpoint separation ($L_{HS}$). The values and their uncertain-
ties of $k_{\text{ox}}$ and $R_{\text{oxs}}$ are from our previous measurements [55]. The thermal conductivity of metal lines ($k_{\text{met}}$) is calculated from the measured electrical resistance according to the Wiedemann-Franz Law. $k_{\text{Si}}$ is well-known data from Ref. [168]. The TBR values and their uncertainties for the graphene/SiO$_2$ interface ($R_{\text{gox}}$) and metal/SiO$_2$ interface ($R_{\text{mox}}$) are based on measurements in Refs. [48] and [45], respectively. These two interface resistances have small contributions to the total uncertainty ($c_i \leq 2\%$) due to their small sensitivities ($s_i$). Even when their TBR values

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<th>Table 4.1: Calculated sensitivities and uncertainty analysis for the extracted graphene $k$ from our measurement at 270 K [correspond to the converged value in Fig. 4.2c with $L_S = 50 \mu\text{m}$ and $L_{\text{probe}} = 1.6 \mu\text{m}$]. The total uncertainty is $\sim 20.8%$.</th>
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<td><strong>Half length of H/S metal lines</strong></td>
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<tr>
<td><strong>Distance of 2 Voltage probes</strong></td>
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<td><strong>Distance of Current and Voltage probes</strong></td>
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change by a factor of 2 (i.e., \( u_{xi}=100\% \)), their contributions become \( c_i = 10\% \) and \( 6\% \), which only changes the total uncertainty from \( \sim 20.8\% \) to \( \sim 23\% \) and \( \sim 21.5\% \), respectively. Thus, their contributions are not shown in the following results.

4.3.2 Optimization of the Platform

The accuracy of our supported thermometry platform can be optimized through two important geometric parameters: i) the center-to-center distance between the heater and sensor (\( L_{HS} \)) and ii) the bottom insulator (here oxide) thickness (\( t_{box} \)) (see Fig. 4.1b). If \( L_{HS} \) is too large then too much of the heater power is dissipated into the substrate; if it is too short, then the temperature drop between heater and sensor is not large compared with the temperature variation under the heater/sensor. If \( t_{box} \) is too thin, significant heat leakage will occur into the substrate; if it is too thick, then its lateral thermal conductance will dominate the heat flow between heater and sensor, overwhelming that of the supported sample.

The optimized values of \( L_{HS} \) and \( t_{box} \) can be found by monitoring the uncertainty change

FIG. 4.4: (a, b) Estimated uncertainty of extracted sample thermal conductivity as a function of the heater-sensor midpoint separation \( L_{HS} \) and the bottom oxide thickness \( t_{box} \), respectively. This gives the optimized design with \( L_{HS} = 600 \text{ nm} \) and \( t_{box} = 300 \text{ nm} \) for the partly-etched sample case (inset of b, red part indicates the sample). (c) Estimated uncertainty of extracted sample \( k \) increases as its thermal sheet conductance \( G_{\circ} \) decreases for \( L_{HS} = 600 \text{ nm} \) and \( t_{box} = 300 \text{ nm} \), showing the measureable \( G_{\circ} \) (blue region) by this SiO$_2$/Si supported thermometry platform. Inset is a schematic for CNT/NW array measurements, where green lines are CNTs/NWs, and red and blue lines are heater and sensor, respectively.
(due to sensitivity change) of extracted sample $k$, and the results are shown in Figs. 4.4a and 4.4b. Here we consider $T = 300$ K and thin film sample of thermal sheet conductance $G_\square = kh = 100$ nWK$^{-1}$, and assume the sample is partly etched off so that only the part between the heater and sensor is preserved (see the inset of Fig. 4.4b). The optimization is calculated at heater and sensor linewidth $D_{\text{met}} = 200$ nm, and only the input parameters whose contributions $c_i$ are larger than 2% are included. From the estimated total uncertainty, we find that the optimized values of $L_{\text{HS}}$ and $t_{\text{box}}$ are ~ 600 nm and ~300 nm, respectively, leading to the minimized uncertainty ~18%. The non-etched case has the similar results but with a slightly higher uncertainty ~25% (see Figs. 4.5a and 4.5b). By looking at the uncertainty contributed by each input parameter, it is clear that the optimization is achieved mainly due to the competition between the measured sensor response ($\Delta T_S$) and the role of the bottom oxide ($k_{\text{ox}}$), as we explained above. Additional calculations (not shown) indicate that narrower heater and sensor linewidths (~100 nm) give almost the same optimized values of $L_{\text{HS}}$ and $t_{\text{box}}$, but slightly lower total uncertainty.

**FIG. 4.5:** Results for the sample non-etched case. (a, b) Optimize the heater-sensor distance $L_{\text{HS}}$ and the bottom oxide thickness $t_{\text{box}}$, respectively. The optimized $L_{\text{HS}}$ and $t_{\text{box}}$ are almost the same as those for the sample non-etched case (Fig. 4.4), but with a slightly higher uncertainty ~25%. (c) Estimated uncertainty of extracted sample $k$ increases as its thermal sheet conductance $G_\square$ decreases for $L_{\text{HS}} = 600$ nm and $t_{\text{box}} = 300$ nm, showing the measureable $G_\square$ within a 50% error (blue region) is $G_\square \geq 32$ nWK$^{-1}$. Inset is a schematic for CNT/NW array measurements, where green lines are CNTs/NWs, and red and blue lines are heater and sensor, respectively.
4.4 Applicability of the Platform

4.4.1 Measureable Thermal Sheet Conductance

After optimizing our supported thermometry platform, the next question concerns the smallest in-plane thermal conductance that can be sensed by this method. To address this, we calculate the uncertainty change of extracted thermal conductivity as a function of the sample thermal sheet conductance $G_{\square} = kh$. When the sample is partly etched to match the dimensions of the heater-sensor width and spacing (inset of Fig. 4.4b) the results at $T = 300$ K are shown in Fig. 4.4c. As expected, the estimated measurement uncertainty increases as $G_{\square}$ decreases. If we set the maximum uncertainty to ~50%, the sensible range of $G_{\square}$ enabled by this platform is $G_{\square} > 25$ nWK$^{-1}$ (the blue region in Fig. 4.4c). For samples that are not etched to conform to the heater-sensor width and separation (e.g., Fig. 4.1a), the uncertainty is slightly higher, and the smallest sensible $G_{\square}$ within a 50% error is ~32 nWK$^{-1}$ (see Fig. 4.5c). This requirement could be satisfied in most thin film materials, such as polymer films ($k > 0.2$ Wm$^{-1}$K$^{-1}$ and $h > 200$ nm) [194] and CNT networks ($k > 20$ Wm$^{-1}$K$^{-1}$ and $h > 2$ nm) [195, 196], etc.

4.4.2 Nanotube or Nanowire Array

We emphasize that this supported thermometry platform can be applied not only to thin films but also to arrays of quasi-one-dimensional materials (inset of Fig. 4.4c). In our previous work [55], we had shown its application to graphene nanoribbon arrays. Here we give estimations of minimum array density required to apply the platform to carbon nanotube and Si nanowire arrays. For single-wall CNT arrays, assuming array density $p$ (the number of CNTs per unit width), the equivalent thermal sheet conductance is $G_{\square} = k(\pi d \delta)p$, where $k$, $d$, and $\delta$ are the thermal conductivity, diameter, and wall thickness of single-wall CNTs, respectively. Then, the array density is given by $p = G_{\square}/(k\pi d \delta)$. Considering single-wall CNTs with $k = 1000$ Wm$^{-1}$K$^{-1}$, $d$
= 2 nm, and $\delta = 0.34$ nm, as well as $G_\square = 25$ nWK$^{-1}$ (the best case), we obtain the density required for CNT array measurements is $p \geq 12$ $\mu m^{-1}$. This CNT array density is achievable experimentally today, as some studies [197, 198] have demonstrated CNT densities up to ~50 $\mu m^{-1}$.

For NW arrays and for thicker multi-wall CNTs the array density is given by $p = G_\square/(k\pi d^2/4)$, where $k$ and $d$ are the thermal conductivity and diameter of the NWs, respectively. For 20 nm diameter Si NWs [77] with $k \approx 7$ Wm$^{-1}$K$^{-1}$, the required array density is $p \geq 11$ $\mu m^{-1}$; for 50 nm diameter Si NWs, smooth and rough edges lead to $k \approx 25$ and 2 Wm$^{-1}$K$^{-1}$, respectively [77, 79], and the required array density is $p \geq 0.5$ $\mu m^{-1}$ and 6 $\mu m^{-1}$. Nanowire arrays can be fabricated much denser than these required densities [78, 199]. The above estimations indicate that the supported thermometry platform can be easily applied to CNT arrays and Si NW arrays with both smooth and rough edges. In addition, such arrays do not require uniform spacing.

4.4.3 Single Si Nanowire

We note that the minimum array density for 50 nm diameter smooth Si NWs is very low (~0.5 $\mu m^{-1}$), which implies that it is possible to measure a single Si NW by using this platform. To confirm this idea, we performed the simulation with just one NW between the heater and sensor (inset of Fig. 4.6a). To achieve the best measurement accuracy, we first optimize the dimensions of the heater and sensor, that is, the midpoint distance between them ($L_{HS}$) and the distance between two voltage probe arms ($D_{PV}$) (inset of Fig. 4.6a). The calculated uncertainty contributed from the measured sensor temperature rise ($\Delta T_S$) as a function of $L_{HS}$ and $D_{PV}$ is shown in Fig. 4.6a. In the calculation, the bottom oxide thickness ($t_{box}$) and electrode linewidth ($D_{met}$, see Fig. 4.1b) are chosen as 300 nm and 200 nm, respectively, and a Si NW with $d = 50$ nm and $k = 25$ Wm$^{-1}$K$^{-1}$ is used. The minimum of the uncertainty indicates the optimized structure is $L_{HS} = 600$ nm and $D_{PV} = 1000$ nm. By using these values, the total uncertainty as a
function of $kA$ ($A$ is the NW cross-sectional area) is calculated and shown in Fig. 4.6b. For highly conductive NWs ($kA > 5 \times 10^{-14}$ WmK$^{-1}$) the measurement uncertainty is around 60%, indicating that obtaining an estimate of the thermal properties of a single NW is possible. However, this also indicates that it is not possible to measure an individual single-wall CNT with the supported platform because its $kA$ is low ($< 2 \times 10^{-14}$ WmK$^{-1}$), although it may be possible to measure one multi-wall CNT as long as the $kA$ condition above is satisfied.

4.4.4 Plastic Substrate

Before concluding, we note that the supported thermometry platform is not limited to SiO$_2$/Si substrates, but could be extended to thermally insulating plastic substrates like Kapton, polyethylene terephthalate (PET) and so on. Here, we consider measurements with a 25 μm thick Kapton substrate on a heat sink (inset of Fig. 4.7a). We note that results for other Kapton thickness or PET are similar. In simulations, the ambient (isothermal) boundary condition should be applied to at least one surface of the substrate, but due to its low thermal conductivity the outer
surfaces of the plastic substrate cannot reach the ambient temperature. Thus, a heat sink with high thermal conductivity is added for this purpose. On the other hand, from a practical viewpoint, measurements are generally performed in vacuum and on a chuck for ambient temperature control, that is, on a heat sink. Since the plastic substrate is generally tens of microns thick, its background thermal conductance will be typically larger than that of the sample; thus the sample should be trimmed (etched) leaving just the portion between the heater and sensor (inset of Fig. 4.7b), otherwise it will be difficult to sense the difference between the sample measurement and the control experiment without the sample, resulting in a large uncertainty. By using \( k_{ps} = 0.37 \text{ Wm}^{-1}\text{K}^{-1} \) for Kapton (DuPont\textsuperscript{TM} Kapton\textregistered MT) and \( G_\square = 100 \text{ nWK}^{-1} \) for the sample, we calculate the measurement uncertainty as a function of the heater-sensor distance \( L_{HS} \), as shown in Fig. 4.7a. The minimized uncertainty is ~ 38\% at \( L_{HS} = 1.2 \text{ µm} \). With this optimized structure, we further calculate the uncertainty change as a function of the sample thermal sheet conductance (Fig. 4.7b), and find the smallest sensible \( G_\square \) within a 50\% error for a

**FIG. 4.7:** (a) Optimizing the heater-sensor midpoint separation \( L_{HS} \) with the platform supported by a plastic substrate on a heat sink (see inset). The estimated uncertainty of extracted sample \( k \) is minimized at \( L_{HS} = 1.2 \text{ µm} \) for a 25 µm thick Kapton substrate. (b) Estimated uncertainty of extracted sample \( k \) increases as its thermal sheet conductance \( G_\square \) decreases, giving the sensible range (blue) of \( G_\square \) by this platform. Inset shows the optimized structure of the platform applied to the plastic substrate, with \( L_{HS} = 1.2 \text{ µm} \) and the sample (red) only between heater and sensor.
Kapton substrate is ~60 nWK\(^{-1}\), which is ~2.5 times higher than for the optimized SiO\(_2\)/Si substrate. Correspondingly, the required density for CNT and NW arrays will be also 2.5 times higher, which remains achievable in experiments.

4.5 Summary

In conclusion, we demonstrated that a relatively simple, substrate-supported platform can be used to measure heat flow in nanoscale samples like graphene, CNT or NW arrays. This platform requires fewer fabrication efforts and is useful for materials which are difficult to suspend, but the sample thermal conductivity must be extracted by 3D finite element analysis. Based on careful uncertainty analysis we find the platform design can be optimized and the smallest thermal sheet conductance measurable by this method within 50% error is estimated to be ~25 nWK\(^{-1}\) at room temperature. This thermometry platform can also be applied to individual nanowires, and can be implemented both on SiO\(_2\)/Si (or similar) and flexible plastic substrates.
CHAPTER 5

BALLISTIC THERMAL CONDUCTANCE AND LENGTH-DEPENDENT SIZE EFFECTS IN LAYERED TWO-DIMENSIONAL MATERIALS

5.1 Introduction

Stimulated by extensive studies of graphene, enormous interest is being generated in the properties of other two-dimensional (2D) layered materials, such as hexagonal boron nitride (h-BN) and transition-metal dichalcogenides (TMDs, e.g., MoS$_2$, and WS$_2$). They exhibit remarkable physical and chemical properties, and are promising candidates for applications in electronics, optoelectronics, and photonics [9, 18, 19, 143]. Understanding thermal properties of materials is important for improving thermally limited performance in devices and efficiency of energy conversion [1, 5, 106]. The thermal properties of these layered materials are unique and highly anisotropic, including high in-plane but very low cross-plane thermal conductivities, due to strong in-plane chemical bonding and weak interlayer van der Waals interactions [23, 24]. Like other materials, as sample dimensions are comparable to the average phonon mean free path (MFP) $\lambda$, size effects of thermal transport become important [5]. However, compared to bulk properties our understanding in this scale is relatively lacking in general (not limited to layered materials).

First, if the sample length $L$ is shorter than average phonon MFP $\lambda$, heat conduction will be ballistic (i.e., no scattering) and governed by an upper limit, ballistic thermal conductance ($G_{\text{ball}}$), but the corresponding values for these layered materials (even for most materials) are still unknown except for graphene [29, 55]. Second, in the range of $L > \lambda$, how thermal conductivity $k$ evolves from the ballistic to diffusive regime as $L$ increases is not well established, and when it will eventually enter the diffusive regime is not clear. Particularly, some theoretical models
predicted that in low-dimensional momentum-conserving systems $k$ will diverge with $L$, i.e., $\sim L^a$ for one-dimension (1D) [200, 201] and $\sim \log L$ for 2D [201-203]. Whereas, in what length scale the divergence might occur and should be experimentally tested has not been carefully discussed.

Third, as an important characteristic length, MFP itself has not been estimated consistently. For example, the “textbook” phonon MFP value for Si is $\sim 40$ nm at room temperature [204], obtained from the kinetic theory by using the sound velocity as phonon group velocity [205]. However, by analyzing accumulative thermal conductivity as a function of MFP, phonons with MFP longer than 1 $\mu$m contribute $\sim 40\%$ to the bulk $k$ in Si [206-209], so a “median” MFP of 0.5-1 $\mu$m is suggested [204]. Thus, it is crucial to systematically study these $L$-dependent size effects as well as the proper estimation of phonon MFP.

In this work, we study ballistic-diffusive thermal conduction in monolayer graphene, $h$-BN, MoS$_2$, and WS$_2$, as well as their three-dimensional (3D) bulk counterparts. Based on full phonon dispersions obtained from $ab$ initio simulations, we calculate the in-plane (for monolayer and bulk) and cross-plane (for bulk) ballistic thermal conductance $G_{\text{ball}}$ of these materials for the first time. Due to their stronger chemical bonding, graphene/graphite and $h$-BN show higher $G_{\text{ball}}$ than MoS$_2$ and WS$_2$ above $\sim 100$ K in general. From our calculated $G_{\text{ball}}$, we can obtain $L$-dependent thermal conductivity by using a phenomenological ballistic-diffusive model, which shows good agreement with very recent measurements [57] of $k$ vs. $L$ up to 9 $\mu$m in suspended graphene. We also show that a proper estimation of the overall MFP $\lambda$ should be a rigorous average of all phonon modes, which can be condensed to an expression just including $G_{\text{ball}}$ and diffusive thermal conductivity $k_{\text{diff}}$. We point out that the kinetic theory can reach the same result as long as the correctly averaged phonon group velocity is used. Importantly, for anisotropic layered materials, 2D and 1D forms of the kinetic theory should be used for in-plane and cross-plane,
respectively. Based on the ballistic-diffusive model, \( k \) eventually converges to its diffusive value, \( k_{\text{diff}} \), around \( L \sim 100\lambda \), much longer than the commonly assumed length. Thus, whether \( k \) is divergent in low-dimensional materials should be examined beyond \( \sim 100\lambda \) to distinguish from the intrinsic increase of \( k \) due to the ballistic-to-diffusive transition. All these results broaden our understanding of thermal transport in low-dimensions and short length scales, and will help guide the use of these layered materials for tailored applications.

### 5.2 Phonon Dispersions by First-Principles Calculations

The equilibrium atomic structures are calculated within density functional theory (DFT) using projector-augmented wave (PAW) potentials \[210\], as implemented in the VASP code \[211\]. The local density approximation (LDA) is used for the exchange-correlation functional \[212\]. The plane-wave basis set with kinetic energy cutoff of 400 eV is used except for \( h\)-BN (450 eV)

![Fig. 5.1: Atomic structures for graphite with AB stacking (a), \( h\)-BN with AA' stacking (b), and TMD with 2H-phase (c), where three atomic layers are plotted for each of them. Gray lines indicate primitive cells for their bulk, and lattice constants \( a \) and \( c \) are labeled. Unrepeatable atoms within the primitive cells are highlighted by bigger and darker colored balls: 4 atoms for graphite and \( h\)-BN, 6 atoms for TMDs. (d) Schematic of their Brillouin zone with high-symmetry lines highlighted. For their 2D monolayers, the material thickness is generally defined as \( c/2 \), and the 2D BZ is simply a regular hexagon (see inset of Fig. 5.2a).](image)
is used). The convergence for energy is chosen as $10^{-8}$ eV between two consecutive steps, and

<table>
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<th>Experiments</th>
<th>DFT simulations</th>
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<td></td>
<td>$a$ (Å)</td>
<td>$c$ (Å)</td>
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<tr>
<td>graphite [26, 213-216]</td>
<td>2.46</td>
<td>6.71</td>
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<tr>
<td>$h$-BN [217, 218]</td>
<td>2.50</td>
<td>6.66</td>
</tr>
<tr>
<td>MoS$_2$ [219]</td>
<td>3.15</td>
<td>12.29</td>
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<tr>
<td>WS$_2$ [220]</td>
<td>3.153</td>
<td>12.323</td>
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**Table 5.1:** Optimized lattice constants from our DFT calculations compared to experimental values from literature [26, 213-220].

**Fig. 5.2:** Calculated phonon dispersions along high-symmetry lines for monolayer graphene (a), $h$-BN (b), MoS$_2$ (c), and WS$_2$ (d). For graphene, red circles [25] and blue triangles [26] are experimental data plotted for comparison. Other experimental data are also shown for $h$-BN [221] and MoS$_2$ [219]. The 2D Brillouin zone for monolayers is shown as the inset in (a).
full geometry relaxation is carried out until remaining forces on atoms smaller than 0.01 eV/Å.

For monolayers, a vacuum spacing of 20 Å is used to prevent interlayer interactions.

After obtaining relaxed lattice constants and atomic structures, the interatomic force constants are calculated within a supercell using the frozen-phonon approach [223]. For graphene/graphite and h-BN, the plane-wave kinetic energy cutoff is increased to 1000 eV, and the supercell size is 5x5x1 and 5x5x2 for their monolayers and bulk, respectively. For MoS$_2$ and WS$_2$, the energy cutoff is still 400 eV, and the supercell size is 7x7x1 and 4x4x3 for their monolayers and bulk, respectively. Last, phonon dispersions are calculated by the PHONOPY
The atomic lattices of bulk graphite, \( h\)-BN, and TMDs are shown in Figs. 5.1a-c. Graphite is well known to crystalize in the AB stacking, while \( h\)-BN favors the AA’ stacking [217, 225]. For TMDs, the most common 2H phase [18, 19] (similar to the AA’ stacking in \( h\)-BN) is considered.
The Brillouin zone (BZ) of their bulk is shown in Fig. 5.1d. Table 5.1 summarizes our relaxed lattice constants, and experimental results [26, 213-220] are listed as well for comparison. Our calculations show that using LDA gives underestimated lattice constants than experimental values, but it gives better agreement with experimental phonon dispersions than using generalized gradient approximation (GGA).

Figure 5.2 shows the calculated phonon dispersions along high-symmetry lines in BZ (see inset) for monolayer graphene, $h$-BN, MoS$_2$ and WS$_2$. The phonon dispersions of their bulk are shown in Fig. 5.3. Our calculations are in excellent agreement with the experimental data [25, 26, 219, 221, 222] plotted as symbols in Figs. 5.2 and 5.3. For monolayer graphene and $h$-BN, there are six phonon branches due to two atoms in their primitive cells (Figs. 5.1a-b); whereas, there are nine phonon branches for monolayer MoS$_2$ and WS$_2$ because of three atoms in their primitive cells (Fig. 5.1c). For the bulk counterparts, each branch in their monolayer phonon dispersions splits into two branches because two layers form a primitive cell in bulk (Fig. 5.1). The two branches are distinguishable on the ΓMK plane, but they become degenerate on the ALH plane in BZ (see Figs. 5.4e-h). Moreover, the dispersion along the cross-plane direction appears in bulk materials (see Fig. 5.4). For cross-plane dispersions along the Γ–A direction, transverse acoustic (TA) and transverse optical (TO') branches are double degenerate, as shown in Figs. 5.4b-d. Interestingly, some high-frequency optical branches ($ZO_1$, $ZO_2$, $LO_1$, $LO_2$) of $h$-BN have significantly nonzero cross-plane group velocity, different from other layered materials, which can be noticed along the $M_1$–$L_1$ direction (Fig. 5.4a) for example (see Figs. 5.4e-h). Thus, when these modes in $h$-BN are excited as temperature $T$ increases, they will provide extra contributions to ballistic thermal conductance $G_{\text{ball}}$, resulting in a “bump” in $G_{\text{ball}}$ versus $T$ of $h$-BN (see Fig. 5.6b).
5.3 Formalism of Thermal Physical Quantities

5.3.1 Heat Capacity

After obtaining full phonon dispersion in the Brillouin zone (BZ), heat capacity can be calculated by

\[ C_v = \frac{1}{V} \sum_{b,q} \hbar \omega^b(\vec{q}) \frac{\partial f}{\partial T}, \quad (5.1) \]

where the material volume \( V = WLH \), a product of width \( W \), length \( L \), and height \( H \); \( \hbar \) is the reduced Planck constant; \( \vec{q} \) and \( \omega^b(\vec{q}) \) are phonon wavevector and frequency \( (b \) denotes different branches), respectively; \( f = 1/(\exp(\hbar \omega^b/k_BT) - 1) \) is the Bose-Einstein distribution; \( T \) is temperature and \( k_B \) is the Boltzmann constant. The sum \( \Sigma \) is over different branches \( (b) \) and all wave vectors \( (\vec{q}) \) in the entire Brillouin zone. In practice, the sum over \( \vec{q} \) is converted to an integral, and the general expressions for one-dimension (1D), two-dimension (2D), and three-dimension (3D) are given by

\[ C_v = \frac{1}{2\pi A} \sum_b \int_{BZ} dq \hbar \omega^b \frac{\partial f}{\partial T}, \quad (1D) \quad (5.2a) \]

\[ C_v = \frac{1}{(2\pi)^2 H} \sum_b \int_{BZ} dq^3 \hbar \omega^b \frac{\partial f}{\partial T}, \quad (2D) \quad (5.2b) \]

\[ C_v = \frac{1}{(2\pi)^3} \sum_b \int_{BZ} dq^3 \hbar \omega^b \frac{\partial f}{\partial T}, \quad (3D) \quad (5.2c) \]

where the integral is calculated in the entire BZ. For 2D and 3D, considering isotropic and anisotropic cases, the expressions change to

\[ C_v = \frac{1}{2\pi H} \sum_b \int dq \hbar \omega^b \frac{\partial f}{\partial T}, \quad \text{(isotropic 2D)} \quad (5.3a) \]

\[ C_v = \frac{1}{2\pi^2} \sum_b \int q^2 dq \hbar \omega^b \frac{\partial f}{\partial T}, \quad \text{(isotropic 3D)} \quad (5.3b) \]
Fig. 5.5: Calculated heat capacity as a function of temperature for graphite (a), h-BN (b), MoS$_2$ (c), and WS$_2$ (d) from Eq. 5.2b (for monolayer) and Eq. 5.2c (for bulk).

\[
C_v = \frac{1}{4\pi^2} \sum_b \int dq_z \int q dq \omega_b \frac{\partial f}{\partial T}, \quad \text{(anisotropic layered 3D)} \quad (5.3c)
\]

These equations will be used in the determination of pre-factors for averaged phonon group velocity \( v \) in Section 5.3.5. Figure 5.5 shows our calculated heat capacity from Eq. 5.2b (monolayer) and Eq. 5.2c (bulk) for graphite, h-BN, MoS$_2$, and WS$_2$.

### 5.3.2 Ballistic Thermal Conductance

Ballistic thermal conductance \( G_{\text{ball}} \) can be calculated from full phonon dispersion without any approximation by

\[
G_{\text{ball}} = \frac{1}{2L} \sum_{b,q} \hbar \omega_b^3 |\mathbf{v}_b(q)| \frac{\partial f}{\partial T}, \quad (5.4)
\]
where \( v_n^b(\bar{q}) = \hat{n} \cdot \nabla_{\bar{q}} \omega_n^b(\bar{q}) \) is phonon group velocity along the direction \( \hat{n} \) (a normalized vector).

After converting the sum to an integral and dividing it by the cross-sectional area \( A = WH \) to get a value independent of material sizes, the general expressions of \( G_{\text{ball}}/A \) for 1D-3D are given by

\[
\frac{G_{\text{ball}}}{A} = \frac{1}{4\pi A} \sum_b \int_{\text{BZ}} dq h \omega_n^b(q) \left| v_n^b(q) \right| \frac{\partial f}{\partial T}, \quad (1D) \tag{5.5a}
\]

\[
\frac{G_{\text{ball}}}{A} = \frac{1}{8\pi^2 H} \sum_b \int_{\text{BZ}} dq^2 h \omega_n^b(\bar{q}) \left| v_n^b(\bar{q}) \right| \frac{\partial f}{\partial T}, \quad (2D) \tag{5.5b}
\]

\[
\frac{G_{\text{ball}}}{A} = \frac{1}{16\pi^3} \sum_b \int_{\text{BZ}} dq^3 h \omega_n^b(\bar{q}) \left| v_n^b(\bar{q}) \right| \frac{\partial f}{\partial T}, \quad (3D) \tag{5.5c}
\]

In our calculations, \( v_x^b(\bar{q}) \) is taken for cross-plane (3D); \( v_x^b(\bar{q}) \) and \( v_y^b(\bar{q}) \) are taken for in-plane (2D and 3D) and they show almost the same results (within 2%), demonstrating the isotropy of in-plane thermal conduction. The average of two results using \( v_x^b(\bar{q}) \) and \( v_y^b(\bar{q}) \) is adopted for in-plane \( G_{\text{ball}}/A \).

For isotropic 2D and 3D, the velocity along a certain direction, \( v_n^b(\bar{q}) \) can be expressed in terms of the radial velocity scalar \( v^b(q) \) as \( v_n^b(q) = v^b(q) \cos \varphi \) and \( v_n^b(q) = v^b(q) \sin \theta \cos \varphi \), respectively, i.e., \( v_n^b(\bar{q}) \) is the projector of \( v^b(q) \) along the direction of temperature gradient. For anisotropic 3D layered materials, we have

\[
v_x^b(q, \bar{q})^2 + v_y^b(q, \bar{q})^2 = v_z^b(q, \bar{q}) \cos \varphi \]

with \( v_z^b(q, \bar{q}) \) as the in-plane velocity scalar, and \( |v_x^b(q, \bar{q})| = v_z^b(q, \bar{q}) \) with \( v_z^b(q, \bar{q}) \) as the cross-plane velocity scalar. Thus, Eq. 5.5b-c in different cases change to

\[
\frac{G_{\text{ball}}}{A} = \frac{1}{8\pi^2 H} \sum_b \int dq d\varphi \int_0^{2\pi} d\psi h \omega_n^b |v^b(q)| \cos \varphi \frac{\partial f}{\partial T}, \quad \text{(isotropic 2D)} \tag{5.6a}
\]

\[
= \frac{1}{2\pi^2 H} \sum_b \int dq dq \omega_n^b v^b(q) \frac{\partial f}{\partial T}
\]

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The equations will be used in the determination of pre-factors for averaged phonon mean free path (MFP) \( \lambda \) and group velocity \( v \) in Sections 5.3.4 and 5.3.5.

### 5.3.3 Diffusive Thermal Conductivity

In the Boltzmann transport equation (BTE) approach with the relaxation time approximation, the diffusive thermal conductivity along a transport direction \( \hat{n} \) is generally given by

\[
     k_{\text{diff}} = \frac{1}{V} \sum_{b, \bar{q}} h \omega_b (\bar{q}) |v^b(\bar{q})|^2 \tau_{\text{tot}}^b (\bar{q}) \frac{\partial f}{\partial T},
\]

where \( \tau_{\text{tot}}^b (\bar{q}) \) is phonon relaxation time. After converting the sum of \( \bar{q} \) to an integral, the general expressions of \( k_{\text{diff}} \) for 1D-3D are then given by

\[
    k_{\text{diff}} = \frac{1}{2\pi A} \sum_b \int_{BZ} dq \, \bar{\omega}_b (q) |v^b(q)|^2 \tau_{\text{tot}}^b (q) \frac{\partial f}{\partial T},
\]

(1D) (5.8a)

\[
    k_{\text{diff}} = \frac{1}{(2\pi)^2 H} \sum_b \int_{BZ} d\bar{q} \, \bar{\omega}_b (\bar{q}) |v^b(\bar{q})|^2 \tau_{\text{tot}}^b (\bar{q}) \frac{\partial f}{\partial T},
\]

(2D) (5.8b)

\[
    k_{\text{diff}} = \frac{1}{(2\pi)^3} \sum_b \int_{BZ} d\bar{q} \, \bar{\omega}_b (\bar{q}) |v^b(\bar{q})|^2 \tau_{\text{tot}}^b (\bar{q}) \frac{\partial f}{\partial T}.
\]

(3D) (5.8c)

For isotropic 1D-3D, phonon MFP is \( \lambda^b(q) = v^b(q) \tau_{\text{tot}}^b \). For anisotropic 3D layered materials, in-
plane and cross-plane phonon MFPs are \( \lambda^b_\parallel (q, q_z) = v^b_\parallel (q, q_z) \tau^b_{\text{tot}} \) and \( \lambda^b_\perp (q, q_z) = v^b_\perp (q, q_z) \tau^b_{\text{tot}} \), respectively. Similar to the treatment of \( v^b_n (\overline{q}) \) in \( G_{\text{ball}}/A \), \( k_{\text{diff}} \) in different cases can be further expressed as

\[
k_{\text{diff}} = \frac{1}{4\pi^2 H} \sum_b \int dq \int_0^{2\pi} d\varphi \omega^b \left[ v^b (q) \cos \varphi \right]^2 \tau^b_{\text{tot}} \frac{\partial f}{\partial T}, \quad \text{(isotropic 2D)} \quad (5.9a)
\]

\[
k_{\text{diff}} = \frac{1}{(2\pi)^3} \sum_b \int dq \int_0^{2\pi} d\varphi \omega^b \left[ v^b (q) \cos \varphi \right]^2 \tau^b_{\text{tot}} \frac{\partial f}{\partial T}, \quad \text{(isotropic 3D)} \quad (5.9b)
\]

\[
k_{\text{diff,}} = \frac{1}{(2\pi)^3} \sum_b \int dq \int_0^{2\pi} d\varphi \omega^b \left[ v^b (q, q_z) \cos \varphi \right]^2 \tau^b_{\text{tot}} \frac{\partial f}{\partial T}, \quad \text{(layered 3D in-plane)} \quad (5.9c)
\]

\[
k_{\text{diff,}} = \frac{1}{(2\pi)^3} \sum_b \int dq \int_0^{2\pi} d\varphi \omega^b \left[ v^b (q, q_z) \cos \varphi \right]^2 \tau^b_{\text{tot}} \frac{\partial f}{\partial T}, \quad \text{(layered 3D cross-plane)} \quad (5.9c)
\]

These equations will be used in the determination of pre-factors for averaged phonon MFP \( \lambda \) in Section 5.3.4.

5.3.4 Averaged Phonon Mean Free Path

If we look at the ratio of \( k_{\text{diff}} \) to \( G_{\text{ball}}/A \), based on Eqs. 5.5a, 5.6, 5.8a, and 5.9, we can find that besides a pre-factor the ratio is just the defined average of phonon MFPs with all modes weighted properly, which is shown below for all cases:

\[
\frac{k_{\text{diff}}}{G_{\text{ball}}/A} = \frac{2 \sum_b \int dq \omega^b |v^b (q)| \lambda^b (q) \frac{\partial f}{\partial T}}{\sum_b \int dq \omega^b |v^b (q)| \frac{\partial f}{\partial T}} = 2 \left\langle \lambda^b (q) \right\rangle = 2\lambda = \lambda_{\text{av}}, \quad \text{(1D)} \quad (5.10a)
\]
\[ \frac{k_{\text{diff}}}{G_{\text{ball}} / A} = \frac{\pi}{2} \sum_b \int_q dq \omega_v^b(q) \lambda_v^b(q) \frac{\partial f}{\partial T} = \frac{\pi}{2} \left\langle \lambda_v^b(q) \right\rangle = \frac{\pi}{2} \lambda = \lambda_{\text{ms}}, \quad \text{(isotropic 2D)} \] (5.10b)

\[ \frac{k_{\text{diff}}}{G_{\text{ball}} / A} = \frac{4}{3} \sum_b \int_q q^2 dq \omega_v^b(q) \lambda_v^b(q) \frac{\partial f}{\partial T} = \frac{4}{3} \left\langle \lambda_v^b(q) \right\rangle = \frac{4}{3} \lambda = \lambda_{\text{ms}}, \quad \text{(isotropic 3D)} \] (5.10c)

\[ \frac{k_{\text{diff} \parallel}}{G_{\text{ball} \parallel} / A} = \frac{\pi}{2} \sum_b \int_{q,z} dq dq \omega_v^b(q,z) \lambda_v^b(q,z) \frac{\partial f}{\partial T} = \frac{\pi}{2} \left\langle \lambda_v^b(q,z) \right\rangle = \frac{\pi}{2} \lambda_{\parallel} = \lambda_{\text{ms}}, \quad \text{(layered 3D in-plane)} \] (5.10d)

\[ \frac{k_{\text{diff} \perp}}{G_{\text{ball} \perp} / A} = 2 \sum_b \int_{q,z} dq dq \omega_v^b(q,z) \lambda_v^b(q,z) \frac{\partial f}{\partial T} = 2 \left\langle \lambda_v^b(q,z) \right\rangle = 2 \lambda_{\perp} = \lambda_{\text{ms}}, \quad \text{(layered 3D cross-plane)} \] (5.10e)

Thus, in general we have

\[ \lambda = \beta_{\parallel} \lambda_{\text{ms}} = \beta_{\parallel} \frac{k_{\text{diff}}}{G_{\text{ball}} / A}, \quad \text{(5.11)} \]

which is the rigorous and correct average of phonon MFPs of all modes. The pre-factor \( \beta_{\parallel} \) is 1/2, 2/\( \pi \), and 3/4 for isotropic 1D, 2D, and 3D materials, consistent with Ref. [175]. Interestingly, for layered 3D materials the in-plane pre-factor is 2/\( \pi \), same as isotropic 2D, and the cross-plane pre-factor is 1/2, same as 1D.

### 5.3.5 Averaged Phonon Group Velocity

When we look at the ratio of \( G_{\text{ball}} / A \) to \( C_v \), based on Eqs. 5.2a, 5.3, 5.5a, and 5.6, we can find that besides a pre-factor the ratio is just the defined average of phonon group velocity with all modes weighted properly, which is shown below for all cases:
Thus, in general we have
\[ v = \beta_v \frac{G_{\text{ball}} / A}{C_v}, \]  
(5.13)

which is the rigorous and correct average of phonon group velocity of all modes. The pre-factor \( \beta_v \) is 2, \( \pi \), and 4 for isotropic 1D, 2D, and 3D materials. Particularly, for layered 3D materials the in-plane and cross-plane pre-factors are \( \pi \) and 2, respectively, similar to the choice of \( \beta_\lambda \). We note that to use Eq. 5.13 the units of \( C_v \) should be JK\(^{-1}\)m\(^{-3}\).

After having averaged phonon MFP \( \lambda \) and group velocity \( v \), we can examine if they can lead
to a consistent result with the kinetic theory. From Eqs. 5.11 and 5.13, we have

\[ k_{\text{diff}} = \frac{1}{d} C_v \nu \lambda = \frac{1}{d} C_v \beta_v \frac{G_{\text{ball}}}{A} \beta_\lambda \frac{k_{\text{diff}}}{G_{\text{ball}}} = \frac{\beta_v \beta_\lambda}{d} k_{\text{diff}}, \tag{5.14} \]

where \( d = 1–3 \) is the material dimension. Based on our derived pre-factors \( \beta_v \) and \( \beta_\lambda \), we find that \( \beta_v \beta_\lambda / d = 1 \) holds for isotropic 1D, 2D, and 3D, meaning the reproduced kinetic theory. Importantly, for anisotropic layered 3D materials \( d \) has to be 2 and 1 for in-plane and cross-plane, respectively, to hold the kinetic theory. This is a very important conclusion which has not been pointed out before.

5.4 Results and Discussion

5.4.1 Ballistic Thermal Conductance

Based on the obtained phonon dispersions, the monolayer and bulk \( G_{\text{ball}}/A \) of layered materials are calculated by Eqs. 5.5b and 5.5c, respectively. The results of \( G_{\text{ball}}/A \) [including monolayer, bulk in-plane (||) and cross-plane (\( \perp \))] as a function of \( T \) for graphene/graphite, \( h \)-BN, MoS\(_2\), and WS\(_2\) are shown in Fig. 5.6. For each material, its monolayer \( G_{\text{ball}}/A \) is higher than that of bulk (||) at low \( T \), but they will become almost overlapped at high \( T \), because the in-plane phonon dispersions of monolayer and bulk are nearly degenerate except at low frequencies. For bulk (\( \perp \)), its \( G_{\text{ball}}/A \) is similar to that of bulk (||) at low \( T \), but the former is about ten times lower than the latter at high \( T \), reflecting the significant anisotropy in heat conduction. For better comparison among four kinds of materials, \( G_{\text{ball}}/A \) of the most widely-used semiconductor material, silicon [174], is also plotted (dashed line) in each panel of Fig. 5.6 as a reference. Above ~100 K, graphene, graphite (||), \( h \)-BN monolayer and bulk (||) show much larger \( G_{\text{ball}}/A \) than Si (Figs. 5.6a-b), due to their very strong in-plane covalent bonds and more dispersive phonon dispersions, whereas, the monolayer and bulk (||) of MoS\(_2\) and WS\(_2\) show smaller \( G_{\text{ball}}/A \).
than Si at $T > 100$ K (Figs. 5.6c-d) due to relatively weak metal-sulfur bonds. All cross-plane $G_{\text{ball}}/A$ of four materials are lower than that of Si because of their weak van der Waals interactions between layers. The room-temperature $G_{\text{ball}}/A$ values and Debye temperature $\Theta_D$ [219, 226, 227] of these materials are listed in Table 5.2.

In the high $T$ limit, all $G_{\text{ball}}/A$ vs. $T$ curves flatten out (saturate) when all phonon modes are fully excited. The temperatures at which $G_{\text{ball}}/A$ reaches 90% of its saturated (maximum) value are nearly the same for the monolayer and bulk (||) of each material. They are $\sim 1150$ K, $\sim 1060$ K, $\sim 320$ K and $\sim 310$ K for graphite, $h$-BN, MoS$_2$ and WS$_2$, respectively, which are roughly 60% of
their Debye temperature $\Theta_D$ (Table 5.2). The corresponding temperatures for bulk (\perp) are \sim 780 K, \sim 1270 K, \sim 345 K and \sim 360 K for graphite, h-BN, MoS$_2$ and WS$_2$, respectively. Interestingly, there is a “bump” in $G_{ball}/A$ of h-BN bulk (\perp) before it flattens out, different from other bulk (\perp) curves. The reason is that the high frequency optical branches (ZO$_1$, ZO$_2$, LO$_1$, LO$_2$) of bulk h-BN have noticeable non-flatten dispersions along the cross-plane direction (see Fig. 5.4f), leading to non-zero phonon velocity $v_z$, unlike the nearly zero $v_z$ in other bulk materials. Thus, when temperature increases and these phonon modes start to contribute to cross-plane conduction, a significant increase (bump) appears in the $G_{ball}/A$ vs. $T$ curve.

In the low $T$ limit, all $G_{ball}/A$ vs. $T$ curves show power law scaling, \sim $T^n$ (Fig. 5.6). For the monolayers, the power exponent is $n \approx 1.59–1.68$, which is a combined effect of $n = 1.5$ from the quadratic ZA branch and $n = 2$ from the linear TA and LA branches [29, 55]. The power law only applies to monolayers below \sim 90 K for graphene and h-BN, and below \sim 40 K for MoS$_2$ and WS$_2$. For bulk (\parallel), the power exponent is $n \approx 2.91–2.96$, which is a combined effect of $n = 2.5$
from the ZA branch (if purely quadratic) [29] and \( n = 3 \) from linear TA and LA branches (see Supporting Information Section 7). The reason that linear TA and LA branches lead to \( n = 3 \) for bulk layered materials can be understood by rewriting Eq. 5.5c as

\[
\frac{G_{\text{ball}}}{A} = \frac{1}{16\pi^3} \sum_b \int d\omega D^b(\omega) \hbar \omega^b \left| \nu_n^b(\omega) \right| \frac{\partial f}{\partial T} \\
= \frac{k_B^2 T}{16\pi^3 n} \sum_b \int dx D^b(\omega) \left| \nu_n^b(\omega) \right| \frac{x^2 e^x}{(e^x - 1)^2},
\] (5.15)

where \( x = \frac{\hbar \omega^b}{k_B T} \) is a dimensionless number. For TA and LA branches at low-frequency, \( \nu_n^b(\omega) \) is constant, and \( D^b(\omega) \propto \omega^2 \) [228], which will give additional \( \sim T^2 \) when the integral is converted to a dimensionless one. Thus, TA and LA branches will have a \( \sim T^3 \) scaling in \( G_{\text{ball}}/A \) at low \( T \).

The reason that the overall \( n \) is closer to 3 than 2.5 is that the real ZA branch for bulk has a linear component (not purely quadratic) at very low frequency [171], resulting in \( n \) larger than 2.5. The power law for bulk (\( || \)) is valid only below \( \sim 35 \) K for graphite and \( h\)-BN, and below \( \sim 20 \) K for MoS\(_2\) and WS\(_2\). For bulk (\( \perp \)), the power exponent is \( n \approx 2.73 - 2.89 \) with the same physical reason as bulk (\( || \)), and it applies only below \( \sim 10 \) K for graphite and \( h\)-BN, and below \( \sim 7 \) K for MoS\(_2\) and WS\(_2\).

Calculated ballistic thermal conductance is a useful quantity in the investigation of heat conduction in materials. It reflects the intrinsic anisotropic conduction and gives the upper limit of heat flow at a certain temperature. Any measured and calculated thermal conductivity \( k \) can be formally converted to \( G/A = k/L \), and compared to \( G_{\text{ball}}/A \), from which we can know if obtained thermal conductivity satisfies the law of quantum mechanics (i.e., below the ballistic limit) [22] and what percentage of ballistic conduction it reaches [55, 57]. More importantly, it can be used to predict thermal conductivity as a function of transport length \( L \) and also to estimate the average phonon MFP \( \lambda \).
5.4.2 Length-Dependent Thermal Conductivity

We first discuss the $L$-dependent thermal conductivity. In the ballistic regime ($L \ll \lambda$), since the conductance rather than the conductivity approaches a constant, the ballistic thermal conductivity $k_{\text{ball}} = (G_{\text{ball}}/A)L$ becomes linearly dependent on length $L$. In the diffusive regime ($L \gg \lambda$), the conductivity is generally independent of length $L$ (the case of $k$ divergent with $L$ will be discussed later), becoming a constant $k_{\text{diff}}$ (diffusive thermal conductivity). Therefore, in the intermediate ballistic-diffusive regime (i.e., quasi-ballistic regime), the thermal conductivity should increase with $L$ and gradually converge to $k_{\text{diff}}$, similar to the mobility change during quasi-ballistic charge transport observed in short-channel transistors [172, 173]. This transition can be captured through a phenomenological model, called ballistic-diffusive (BD) or quasi-ballistic (QB) model [55, 171]:

$$k(L) = \left[ \frac{1}{(G_{\text{ball}}/A)L} + \frac{1}{k_{\text{diff}}} \right]^{-1} \approx \sum_b \left[ \frac{1}{(G_{\text{ball}}^b/A)L} + \frac{1}{k_{\text{diff}}^b} \right]^{-1},$$

(5.16)

where the first expression is a “1-color” model, and the second one is a branch-resolved “multi-color” model taking into account different phonon branch contributions separately. Apparently, such $L$-dependent $k$ expressions can correctly reproduce both ballistic and diffusive regimes stated above. As we will show later, this model is essentially a Landauer-like model and it can yield an expression of diffusive thermal conductivity consistent with the kinetic theory.

We first apply this model to the thermal conductivity of graphene supported on SiO$_2$. Figure 5.7a shows its $k$ ($T=300$ K) as a function of $L$ from both experimental measurements [49, 55, 229] (solid symbols) and Boltzmann transport equation (BTE) calculations (open symbols, calculations follow the method described in Ref. [49], including the use of an empirical potential to describe the atomic interactions). By using our calculated $G_{\text{ball}}/A = \Sigma_b G_{\text{ball}}^b/A = 4.37$ GW K$^{-1}$ m$^{-2}$
for graphene as well as $k_{\text{diff}} = \Sigma_b k_{\text{diff}}^b = 578 \text{ Wm}^{-1}\text{K}^{-1}$ from BTE simulations, the 1-color model (solid blue line) and 6-color model (solid orange line) as well as its components of each branch (dash-dot lines) are shown in Fig. 5.7a. They are in good agreement with experimental data and BTE simulations, indicating that the BD model can provide reasonable $L$-dependent $k$ in the intermediate regime. We find that the simple 1-color model is sufficiently good to give almost the same result as the 6-color model, although the latter provides more information about the contribution of each branch. For supported graphene, besides three acoustic branches, the flexural optical (ZO) branch also has a notable contribution, but other optical (TO and LO) branches have negligible contributions ($<1\%$). This is because the ZO branch has relatively low phonon frequency, and hence larger thermal population.

We have demonstrated the BD model can successfully describe the $k$ change with $L$ in supported graphene, next we focus on the $L$-dependent $k$ in suspended graphene. Since graphene is a 2D material, and some theoretical studies predicted in isolated low-dimensional (1D and 2D) momentum-conserving systems $k$ will diverge with $L$, i.e., $\sim L^a$ for 1D [200, 201] and $\sim \log L$ for 2D [201–203]. However, other works [85, 230, 231] argued that disorder and higher-order three-phonon scattering may eliminate the divergence, and no experiments have confidently observed divergent $k$ yet. For supported graphene discussed above, the $\sim \log L$ divergence does not appear due to phonon scattering with substrate vibrational modes [97, 98], but for suspended graphene it is still an open question.

Very recently, Xu et al. [57] systematically measured $k$ of suspended graphene as a function of $L$, and their data at $T=300$ K (green squares) are shown in Fig. 5.7b. We find that our 1-color BD model (Eq. 5.16) can fit their data well with the fitting parameter $k_{\text{diff}} = 1790 \text{ Wm}^{-1}\text{K}^{-1}$ (see solid line in Fig. 5.7b). If assuming the divergence of $k \sim \log L$ for large $L$, the BD model can be
changed by adding a logarithmic term to capture this effect:

$$k(L) = \left[ \frac{1}{(G_{\text{ball}} / A)L} + \frac{1}{k_{\text{diff}} + k_0 \ln(L / L_0 + 1)} \right]^{-1}, \quad (5.17)$$
where \( k_0 \) and \( L_0 \) are parameters with units of thermal conductivity and length, respectively. We call this model as the “log model A” and it can reproduce the ballistic limit correctly as well, i.e., \( k \to (G_{\text{ball}}/A)L \) when \( L \to 0 \). By choosing \( k_{\text{diff}} = 1590 \text{ Wm}^{-1}\text{K}^{-1} \), \( k_0 = 130 \text{ Wm}^{-1}\text{K}^{-1} \), and \( L_0 = 1.1 \mu \text{m} \), the log model A can also fit the data of Xu et al. [57] well (see dash-dot line in Fig. 5.7b). Here we also propose another log model B:

\[
k(L) = \frac{G_{\text{ball}}}{A} L_B \ln \left( \frac{L}{L_B} + 1 \right),
\]

(5.18)

where \( L_B \) is a length parameter. Similar to the log model A, the log model B can also reproduce the correct ballistic behavior at short \( L \), that is, \( k \to (G_{\text{ball}}/A)L \) when \( L \to 0 \). The best fit of this model to experimental data of Xu et al. [57] by using \( L_B = 100 \text{ nm} \) is shown as the dot line in Fig. 5.7b. The fit of the log model B is not as good as that of the log model A, but both are worth to be employed and tested. It is clear that the convergent BD model and divergent log model A are distinguishable only at \( L > 10 \mu \text{m} \), and below 10 \( \mu \text{m} \) the increase of \( k \) with \( L \) mainly results from the ballistic-to-diffusive transition (or quasi-ballistic effect). However, currently available data of \( k \) are only up to 9 \( \mu \text{m} \), so further measurements beyond 10 \( \mu \text{m} \) are required to eventually show whether thermal conductivity is divergent in suspended graphene. For 1D it is predicted that \( k \) diverges with \( L \) as \( \sim L^\alpha \), so similar to Eq. 5.17 we propose divergent \( k(L) \) with a power law term for 1D:

\[
k(L) = \left[ \frac{1}{(G_{\text{ball}}/A)L} + \frac{1}{k_{\text{diff}} + \gamma L^\alpha} \right]^{-1},
\]

(5.19)

where \( k_{\text{diff}}, \gamma, \) and \( \alpha \) can be fitting parameters to fit experimental data or theoretical calculations.

In Fig. 5.7c we also plot experimental thermal conductivity data [72, 83, 232, 233] for suspended single-wall carbon nanotubes (SWCNTs) with similar diameters as a function of length at room temperature. There is no systematic measurement of \( k \) versus \( L \) for SWCNTs, and the
few available data do not fall in a single trend, so here we only use the 1-color BD model (Eq. 5.16) to fit to individual data points (dash-dot lines) and give a “band” (yellow area) to show the $k$ range as $L$ increases (Fig. 5.7c). As shown by Mingo and Broido [29], SWCNTs have the same $G_{\text{ball}}/A$ as graphene above $\sim$200 K, so the used room temperature $G_{\text{ball}}/A$ for SWCNTs is 4.37 GWK$^{-1}$m$^{-2}$ (same as graphene) in the BD model. The range of obtained $k_{\text{diff}}$ is $\sim$2500–8500 Wm$^{-1}$K$^{-1}$, and thermal conductivity keeps increasing with length up to tens of microns. A more general expression of $k$ including both length and temperature dependence for SWCNTs is provided in our previous study of short channel ($L < 100$ nm) CNT devices [193], where heat conduction is nearly ballistic.

For graphite, h-BN, MoS$_2$, and Si, their $L$-dependent $k$ at 300 K obtained from the 1-color BD model are summarized in Fig. 5.7d, including monolayer (1L), bulk in-plane ($\parallel$) and bulk cross-plane ($\perp$) $k$ of each material where the corresponding measured $k_{\text{diff}}$ are known. For suspended graphene, most Raman measurements report $k$ in the range of $\sim$2000–4000 Wm$^{-1}$K$^{-1}$ for $L \sim 1$–10 $\mu$m [23, 24], so here we use $k_{\text{diff}} = 4000$ Wm$^{-1}$K$^{-1}$ in the BD model to plot its $L$-dependent $k$ if assuming convergent $k(L)$. In Fig. 5.7d, other $k_{\text{diff}}$ used in the BD model are all from experimental measurements in the literature: $k_{\text{diff}} = 2000$, 6, 400, 2, 35, 2.5, and 150 Wm$^{-1}$K$^{-1}$ for graphite ($\parallel$) [82], graphite ($\perp$) [82], h-BN ($\parallel$) [234], h-BN ($\perp$) [235], MoS$_2$ (1L) [236], MoS$_2$ ($\perp$) [237], and Si [168], respectively. These layered materials show a strong anisotropy in thermal conductivity, and their values span a wide range, more than three orders of magnitude. The estimated $k$-$L$ dependence given here will be helpful for understanding heat conduction at scales where size effects take place.

5.4.3 Estimation of Average Phonon Mean Free Path

Next we turn to the estimation of phonon MFP $\lambda$ in terms of the calculated $G_{\text{ball}}/A$. We note
that the underlying physics of the BD model is Landauer transport theory, in which the conductance (or conductivity) is given by the ballistic conductance (or conductivity) multiplied by a transmission coefficient \[24, 174, 238]\):

\[
k(L) = \frac{G_{\text{ball}}}{A} L \left( \frac{\lambda_{\text{bs}}}{L + \lambda_{\text{qs}}} \right) = \left[ \frac{1}{(G_{\text{ball}}/A)L} + \frac{1}{k_{\text{diff}}} \right]^{-1},
\]

(5.20)

where the transmission coefficient is given in terms of the transport length \(L\) and averaged phonon back-scattering MFP \(\lambda_{\text{bs}}\), that is, \(\lambda_{\text{bs}}/(L+\lambda_{\text{bs}})\). A simple rearrangement of the first expression will reproduce the BD model, meanwhile yielding a relation \(\lambda_{\text{bs}} = k_{\text{diff}}(G_{\text{ball}}/A)\). This relation can be directly derived from the definition of averaged phonon MFP with all modes weighted properly (see Section 5.3.4). The common phonon MFP \(\lambda\) is shorter than the back-scattering MFP \(\lambda_{\text{bs}}\), and they are related with a factor \(\beta_{\lambda}\), as shown by Eq. 5.11.

As long as we know reliable \(k_{\text{diff}}\) from calculations or experimental measurements, the overall phonon MFP can be estimated based on Eq. 5.11, because \(G_{\text{ball}}/A\) can be calculated without approximations. Take graphite as an example, using its widely-accepted values of measured \(k_{\text{diff}}\) \[23, 82\] and our calculated \(G_{\text{ball}}/A\), the obtained phonon in-plane and cross-plane MFPs (\(\lambda_{||}\) and \(\lambda_{\perp}\)) as a function of temperature are shown as solid lines in Fig. 5.8a. They decrease rapidly as \(T\) increases and differ by two and one orders of magnitude at low and high \(T\), respectively. At room temperature, \(\lambda_{||} = 290\) nm and \(\lambda_{\perp} = 10\) nm. The latter corresponds to \(~30\)-layers thickness in graphite, which means the cross-plane heat conduction in multi-layer graphene is already in the ballistic regime. Thus, the advantage of the single average MFP (Eq. 5.11) is giving information in a concise way, compared to mode-dependent MFPs, and it helps us understand when to consider size effects and make corrections to thermal conductivity in a simple way, which is quite useful especially from a device point of view.
We point out that the traditional way to estimate average phonon MFP is through the kinetic theory, \( k_{\text{diff}} = \frac{1}{d} C_v v \lambda \), where \( d = 1-3 \) is the material dimension, \( C_v \) is the heat capacity, and \( v \) is the average phonon group velocity. Different from Eq. 5.11, using this method requires not only \( k_{\text{diff}} \) and \( C_v \) but also careful calculations for averaged values of phonon group velocity \( v \). However, most studies simply used the sound velocity \( v_s \) (low-frequency group velocity) averaged among acoustic branches as \( v \). This will underestimate phonon MFP for two reasons. First, the sound velocity is only valid for low-frequency phonons and hence for low \( T \). For high \( T \), even room temperature, the effective group velocity is much smaller. Second, for the flexural ZA mode in layered materials, its low-frequency group velocity approaches zero, and cannot be simply included in the usual way [239]. Thus, only including TA and LA modes will overestimate \( v \).

Take graphite as an example, through the sound velocity average [239], we have \( v_\parallel = \frac{2}{v_s^\text{TA} + v_s^\text{LA}} \) \( \approx 15.8 \) km/s and \( v_\perp = \frac{3}{2 v_s^\text{TA} + v_s^\text{LA}} \) \( \approx 2.0 \) km/s, where \( v_s^\text{TA}, v_s^\text{LA}, v_s^\text{TA}, v_s^\text{LA} \).
and $v^{LA}_{s,\perp}$ are from our calculated phonon dispersion. Using these values with $C_v$ from our calculations (see Section 5.3.1) and $k_{\text{diff}}$ given previously, the obtained $\lambda_||$ and $\lambda_{\perp}$ as a function of temperature from the kinetic theory are shown as dash lines in Fig. 5.8a. We note that since graphite is anisotropic, the equations for in-plane and cross-plane should be taken as 2D ($d=2$) and 1D ($d=1$) forms of the kinetic theory, respectively, similar to the choice of $\beta$ (shown in Section 5.3.5). As expected, the obtained $\lambda_|| (=145 \text{ nm at 300 K})$ from the kinetic theory is lower than that from our method (Eq. 5.11) over the whole $T$ range, mainly due to neglecting the small group velocity of ZA mode in the average. The $\lambda_{\perp} (=1.7 \text{ nm at 300 K})$ from the kinetic theory is also underestimated, except for low $T$ ($<30 \text{ K}$), the range in which the sound velocity is valid. The consistence between two methods for $\lambda_{\perp}$ at low $T$ also indicates that the 1D form of the kinetic theory for cross-plane is correct.

To obtain correct average phonon MFP $\lambda$ by the kinetic theory, the group velocity $v$ should be an average weighted by the heat capacity, as shown by Eq. 5.13 in Section 5.3.5. Substituting Eq. 5.13 into the kinetic theory, the phonon MFP is then given by

$$\lambda = \frac{k_{\text{diff}} d}{C_v v} = \frac{d}{\beta_v G_{\text{ball}} / A}. \quad (5.21)$$

We can find $d/\beta_v \equiv \beta_\perp$ for all cases, so when the correct $v$ is used, the kinetic theory can give the same estimation of MFP as our model (Eq. 5.11). Figure 5.9a shows the calculated $v$ in terms of Eq. 5.13 as a function of $T$ for graphene, graphite ($||$), and graphite ($\perp$). In the whole temperature range, the maximum of $v$ for graphite ($||$) and graphene is $\sim 8 \text{ km/s}$, about two times smaller than the averaged sound velocity shown above (15.8 km/s). For graphite ($\perp$), the averaged $v$ at 300 K is only $\sim 345 \text{ m/s}$, almost six times smaller than 2 km/s from the sound velocity average, and it reaches 2 km/s only below $\sim 30 \text{ K}$, i.e., the $T$ range where the sound velocity is valid. The calcu-
After demonstrating the BD model and kinetic theory are consistent in the MFP estimation, we apply Eq. 5.11 to other interesting materials whose measured $k_{\text{diff}}$ are available. As shown in Fig. 5.8b, the estimated $\lambda$ at 300 K are ~3, 9, 10, 25, 70, 90, 100, 290, 580 nm for $h$-BN ($\perp$), MoS$_2$ ($\perp$), graphite ($\perp$), MoS$_2$ (1L), $h$-BN ($||$), graphene (on SiO$_2$), Si, graphite ($||$), and graphene (suspended), respectively. The used $k_{\text{diff}}$ are listed previously. We note that Eq. 5.11 gives the “averaged” MFP including contributions from all phonon modes, but some modes (e.g., optical) have very small contributions to thermal conductivity (heat conduction) and very short MFPs.

Fig. 5.9: Calculated phonon group velocity as a function of temperature for graphite (a), $h$-BN (b), MoS$_2$ (c), and WS$_2$ (d) from Eq. 5.13. Each material includes its monolayer, bulk ($||$), and bulk ($\perp$).
(<10 nm for in-plane and <1 nm for cross-plane). This means that those modes contributing to heat conduction significantly should have MFPs longer than the value given by Eq. 5.11. Indeed, by analyzing accumulative thermal conductivity as a function of MFP, it is found that phonons with MFP longer than 1 µm and 100 nm contribute ~40% to the total thermal conductivity for Si [206-209] and cross-plane graphite [240] at 300 K, respectively. Thus, a “median” MFP of 0.5-1 µm and ~100 nm (much larger than our “averaged” numbers, 100 nm and 10 nm) is suggested to explain the strong size effects of thermal transport in Si membrane [204] and graphite (cross-plane) [240], respectively. However, we emphasize that the value given by Eq. 5.11 is a rigorous average with all phonon modes weighted properly (see Section 5.3.4) to represent the overall MFP, which should be used in the kinetic theory and to understand quasi-ballistic thermal transport. By comparing our estimated MFPs in Fig. 5.8b and $k(L)$ in Fig. 5.7d, we can find that when $L < \lambda$, heat conduction enters the ballistic regime (i.e., the linear region in Fig. 5.7d) as expected. Whereas, when $L$ is shorter than the suggested “median” MFP (~10λ), $k$ just starts to decrease rapidly, but is not in the ballistic regime, meaning the suggested “median” MFP is more like a characteristic length below which the size effects (not ballistic transport) take place. Interestingly, beyond 10λ thermal conductivity still increases slowly and will eventually reach $k_{\text{diff}}$ (i.e., become fully diffusive) at $L \sim 100\lambda$ (Fig. 5.7d), which is much longer than the commonly assumed length. The whole ballistic-to-diffusive transition takes more than two orders of magnitude in length ($\lambda$-100λ) to complete. This also indicates that any obtained $k$ increase in this range might arise from the intrinsic ballistic-to-diffusive transition, and whether $k$ is divergent in low-dimensional materials should be examined beyond 100λ to draw a realistic conclusion.

5.5 Summary

In conclusion, we calculated the ballistic thermal conductances $G_{\text{ball}}$ of graphene/graphite, $h$-
BN, MoS$_2$, and WS$_2$ based on full phonon dispersions obtained from ab initio simulations. From the calculated $G_{\text{ball}}$, we obtained $L$-dependent $k$ by using a phenomenological ballistic-diffusive model. In particular, for suspended graphene recent measurements [57] of $k$ vs. $L$ can be fitted by both the convergent BD model and divergent log model, and the two models only differ beyond $L\sim10\ \mu$m. We also showed that the rigorously averaged phonon MFP $\lambda$ is simply determined by $G_{\text{ball}}$ and $k_{\text{diff}}$, and that the kinetic theory can reach the same result as long as a proper phonon group velocity is used. We emphasize that for anisotropic layered materials, 2D and 1D forms of the kinetic theory should be used for in-plane and cross-plane, respectively. Based on the calculated $\lambda$ and the BD model, we find that $k$ will not fully converge to $k_{\text{diff}}$ until after $L\sim100\lambda$, much longer than the commonly assumed length. Thus, to verify predictions of divergent $k$ in low-dimensional systems, simulations and measurements should be performed beyond $L\sim100\lambda$. 
CHAPTER 6
CONCLUSIONS AND OUTLOOK

6.1 Conclusions

In this dissertation, we investigated thermal transport in graphene and several other 2D layered materials, with a focus on nanoscale ballistic conduction and size effects. We combined experimental measurements, finite element simulations, and theoretical calculations to give a comprehensive study.

First, we measured heat conduction in nanoscale graphene by a substrate-supported thermometry platform. Short, quarter-micron graphene samples reach ~35% of the ballistic thermal conductance limit up to room temperature. In contrast, patterning similar samples into nanoribbons (GNRs) leads to a diffusive heat flow regime that is controlled by ribbon width and edge disorder. In the edge-controlled regime, the GNR thermal conductivity scales with width approximately as \(\sim W^{1.8\pm0.3}\), being about 100 Wm\(^{-1}\)K\(^{-1}\) in 65-nm-wide GNRs, at room temperature. Thus, the usual meaning of thermal conductivity must be carefully interpreted when it becomes a function of sample dimensions. These findings are highly relevant for all nanoscale graphene devices and interconnects, also suggesting new avenues to manipulate thermal transport in 2D and quasi-one-dimensional systems.

We also examined the possibility of using this supported platform to measure other materials through finite element simulations. The platform geometry is optimized based on uncertainty analysis. The smallest thermal sheet conductance that can be sensed by this method within a 50% error is \(\sim25\) nWK\(^{-1}\) at room temperature, indicating this platform can be applied to most thin films like polymer and nanotube networks, as well as nanomaterials like nanotube/nanowire arrays, even a single Si nanowire. Moreover, the platform can also be extended to plastic sub-
strates (not limited to the SiO$_2$/Si substrate), and could find wide applicability in circumstances where fabrication challenges and low yield associated with suspended platforms must be avoided.

Last, we calculated in-plane (for monolayer and bulk) and cross-plane (for bulk) ballistic thermal conductances $G_{\text{ball}}$ of graphene/graphite, $h$-BN, MoS$_2$, and WS$_2$, based on full phonon dispersions from first-principles approach. We find that the anisotropy of thermal transport in these materials comes from both anisotropic $G_{\text{ball}}$ and phonon MFPs, not just the effect of one of them. A proper estimation of the overall MFP $\lambda$ should be a rigorous average of all phonon modes, which can be condensed to an expression just including $G_{\text{ball}}$ and diffusive thermal conductivity $k_{\text{diff}}$. We point out that the kinetic theory can reach the same result as long as the correctly averaged phonon group velocity is used. We emphasize that for anisotropic layered materials, 2D and 1D forms of the kinetic theory should be used for in-plane and cross-plane, respectively. Based on the calculated $\lambda$ and the BD model, we find that $k$ will not fully converge to $k_{\text{diff}}$ until after $L \sim 100\lambda$, much longer than the commonly assumed length. Thus, to verify predictions of divergent $k$ in low-dimensional systems, simulations and measurements should be performed beyond $L \sim 100\lambda$ to distinguish from the intrinsic increase of $k$ due to the ballistic-to-diffusive transition.

These results represented a comprehensive study of thermal conduction in 2D layered materials in micro and nanoscale where ballistic conduction and size effects take place. We extended experimental methods to measure nanoscale thermal conduction and showed that thermal conductivity should be redefined in nanoscale and could be tuned effectively. This dissertation broadens our understanding of thermal conduction and how to manipulate it to reach the requirements for potential applications like thermal management and thermoelectric conversion.
6.2 Future Work

There has been an increasing interest of thermoelectric properties in low-dimensional nanostructures. Thermoelectric transport of graphene has been experimentally studied, showing a maximum Seebeck coefficient of $S \sim 100 \mu\text{V/K}$ at room temperature (Section 2.4). However, the thermoelectric properties of GNRs are still unknown in experiments. As pointed out in Section 3.4.4, in the intermediate width range of GNRs ($40 \text{ nm} < W < 200 \text{ nm}$), compared with graphene, GNR thermal conductivity $k$ is suppressed significantly while electrical conductivity $\sigma$ is not affected. Thus, GNRs may have higher $ZT$ than graphene. The Seebeck coefficient of GNRs is suggested to be measured to investigate the effects of carrier density and edge scattering on their thermoelectric properties, which will be useful for potential applications in thermoelectric devices and energy conversion.

Besides graphene, other 2D materials like h-BN and TMDs also show outstanding electrical properties and promising applications in electronics and optoelectronics. They attracted a lot of studies about its electronic transport properties, but few focused on their thermal properties. Although our current study has extended to the thermal transport of these 2D materials in a theoretical frame (Chapter 5), there are very few experimental works available in the community. Therefore, it is crucial to measure thermal conduction of these materials in the future, which will help to better understand the performance of devices made of them. In addition, TMDs are predicted to have higher thermopower than graphene due to the presence of band gaps, so their thermoelectric properties are worth to investigate experimentally.

As mentioned in Chapter 5, whether thermal conductivity diverges with transport length in low-dimensional materials is still an open question. To clarify this issue, experimental measurements should be carried out on 1D and 2D materials with length beyond $\sim 100$ times of their
phonon MFP. Furthermore, studying the thermal rectification effect of nanostructures composed of 2D materials is important and helpful to develop thermal diodes and phononics in the future.
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