Thermal Transport Across 2D/3D Van Der Waals Interfaces

Cameron Foss

University of Massachusetts Amherst

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THERMAL TRANSPORT ACROSS 2D/3D VAN DER WAALS INTERFACES

A Dissertation Presented
by
CAMERON FOSS

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY
February 2023
Electrical and Computer Engineering
THERMAL TRANSPORT ACROSS 2D/3D VAN DER WAALS INTERFACES

A Dissertation Presented

by

CAMERON FOSS

Approved as to style and content by:

________________________________________
Zlatan Aksamija, Chair

________________________________________
Eric Polizzi, Member

________________________________________
Neal Anderson, Member

________________________________________
Ashwin Ramasubramaniam, Member

Christopher V. Hollot, Department Head
Electrical and Computer Engineering
DEDICATION

This dissertation is dedicated to

My parents who have raised me to be the person I am today

My friends who have made these years memorable
ACKNOWLEDGMENTS

I will be ever grateful to my research advisor, Prof. Zlatan Aksamija, for his exceptional guidance and mentorship. I would like to thank Prof. Eric Polizzi and Prof. Neal Anderson for not only serving on my dissertation committee, but for being tremendous teachers as well. A special thanks to Prof. Ashwin Ramasubramaniam for serving as the external member of my dissertation committee. Lastly, I would like to thank my labmates, friends, and family for their unwaivering support.
ABSTRACT

THERMAL TRANSPORT ACROSS 2D/3D VAN DER WAALS INTERFACES

FEBRUARY 2023

CAMERON FOSS
B.S., UNIVERSITY OF MASSACHUSETTS AMHERST
M.S.E.C.E., UNIVERSITY OF MASSACHUSETTS AMHERST
Ph.D., UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professor Zlatan Aksamija

Designing improved field-effect-transistors (FETs) that are mass-producible and meet the fabrication standards set by legacy silicon CMOS manufacturing is required for pushing the microelectronics industry into further enhanced technological generations. Historically, the downscaling of feature sizes in FETs has enabled improved performance, reduced power consumption, and increased packing density in microelectronics for several decades. However, many are claiming Moore’s law no longer applies as the era of silicon CMOS scaling potentially nears its end with designs approaching fundamental atomic-scale limits – that is, the few- to sub-nanometer range. Ultrathin two-dimensional (2D) materials present a new paradigm of materials science and may pave the way for beyond-silicon CMOS technologies. Since the exfoliation of semi-metallic graphene in 2004, there have been discoveries of new families of semiconducting and insulating 2D materials that help realize fully-2D-based platforms, the study of novel quantum device physics, and provide
new avenues in sensing and optical applications. However, selecting a new semiconducting channel material to design around is a highly non-trivial problem which requires finding a superlative candidate and then surrounding it with appropriate contacts (e.g., substrate) to ensure optimal performance. In modern microelectronics, a key feature for reliable performance is high interface thermal conductances so waste heat generated in device hot spots has a low-resistance pathway to thermal management hardware. Despite that importance, the study of interface thermal conductance between prospect 2D materials and their surrounding 3D contacts remains far behind the vast amount of literature covering their electrical and optical properties. This dissertation investigates interface thermal transport across mixed-dimensional van der Waals 2D/3D interfaces using a phonon Boltzmann transport model. In general, amorphous substrates which display a low-energy peak in their vibrational density of states, called the *boson peak*, have higher TBC than interfaces with crystalline substrates. The composition of the substrate can impact where the boson peak occurs, and a lower boson peak location can greatly improve the TBC for most interface pairings. For example, the boson peak occurs at 10 meV for SiO$_2$ as compared to 20 meV for AlO$_x$, and as a result the TBC of 2D/SiO$_2$ interfaces are either equivalent to or better (by a factor of 1.33 or 2 in certain cases) than 2D/AlO$_x$ interfaces. It is later shown that the TBC for bare 2D/3D interfaces can be bottlenecked by internal resistance that depends on the anharmonic processes of the 2D-layer. It is shown that encapsulation can lift this bottleneck, increasing TBC and reducing the temperature dependence by aiding in ZA phonon replenishment. It is further shown that several beyond-graphene materials, such as silicene and BAs, may have a TBC higher than that of graphene and hBN. Machine learning applied to a dataset comprised of 156 unique interface pairings reveals that the TBC depends strongly on select material (or interface) properties, such as the vdW spring coupling constant, 2D thermal conductivity, flexural phonon bandwidth, vdW resonant gap, and the frequency of the first peak in the substrate vDOS. Lastly, the TBC is shown to in-
crease with increasing 2D-layer thickness and including hBN as a bottom-layer in 2D vdW heterostructured stacks can improve the TBC by a factor of 2 or 3 up to 150 MW.m$^{-2}$.K$^{-1}$. 
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CHAPTER 1
INTRODUCTION

The long-established trend of downscaling microelectronics has brought continued progress in computational speed and data storage for several decades. To sustain trends in scaling, the standard planar-silicon-MOSFET has gone through several design modifications. Si-Ge alloys were used to apply channel strain to increase carrier mobility [11, 12]. High-$k$ dielectric oxides [13] and FinFET/FinFET-inspired structures (e.g., gate-all-around, multi-gate) [14, 15] have further provided enhanced control over gate-channel electrostatics for overcoming numerous short-channel effects [16]. These advancements have been tremendously successful in carrying integrated circuits (ICs) into sub-5nm technological nodes, however there are fundamental physical limits to how far silicon CMOS-based devices can be scaled. Facing those limitations, researchers have turned to novel quantum physics (e.g., spintronics, tunnel FETs, etc.) and new nanoscaled material platforms (i.e., 2D and 1D systems) in exploring avenues toward next-generation post-silicon CMOS transistors and microelectronics. However, despite decades of research it is still unclear whether silicon will continue to dominate or if a new disruptive semiconducting material will supplant it.

Isolated single- and few-layer Van der Waals (vdW) two-dimensional (2D) materials provide a platform of mechanically flexible and atomically thin materials that can act as building blocks for next-generation electronics [17, 18, 19, 20]. Bulk vdW materials represent a class of compounds that are covalently bonded in their in-plane (or xy-) directions but have vdW bonding in their cross-plane (or z-) direction (e.g., see graphite in Fig. 1.1a). Van der Waals bonds are much weaker than covalent bonds, and therefore single-layers can be
mechanically exfoliated from their many-layered assemblies (e.g., graphene from graphite [21]) and transferred to various substrate handles with less concern for lattice commensurability [22, 23, 24]. Further, due to the weak vdW bonding in the cross-plane direction, there is often significant anisotropy between in-plane and cross-plane energy transport in vdW materials [25] which can be utilized to control the flow of energy at the nanoscale.

Subsequent to the discovery of graphene in 2004 [21, 26], 2D materials comprised of group IV, V, and III-V elements that exhibit inherently metallic, semiconducting, and insulating properties have attracted tremendous interest [27]. The most notable are group IV graphene-like hexagonal materials such as silicene (see Fig. 1.2) and germanene which support massless dirac-fermions and show potential as topological insulators [28, 29, 30]. Further beyond graphene analogues which are mostly semi-metals, boron arsenide (BAs) and (blue and black) phosphorene have been emerging as promising semiconductors [31, 32] with exceptionally large carrier mobilities [33, 34]. Other notable 2D materials are semiconducting 1H-phase transition metal dichalcogenides (TMDs) (shown in top-right of Fig. 1.2) and insulating hexagonal boron nitride (BN). Beyond the wide-range of physical

Figure 1.1: The crystal structures of graphite in its AB-stacking form and single-layer graphene are shown. All atomic structures are visualized using the crystal visualization software XCrySDen [1].
properties that 2D materials provide as isolated single-layered systems, these materials can also be rearranged and stacked into vertical heterostructures (see bottom-right of Fig. 1.2) that have been shown to display physical features superior to or not present in the individual constituent materials [35, 36, 37, 38]. For example, GaN/BNs 2D heterostructures exhibit a small direct band gap (0.676 eV) [39], while single-layer 2D GaN has a large (2.36 eV) indirect band gap [40].

With these advances, 2D materials show exciting promise in future applications of optoelectronics, sensing, and field-effect-transistors [41, 42, 43, 44, 20], while potentially enabling higher packing densities than their 3D counterparts [45]. However, modern high-performance electronics rely on materials with not only tailored electrical and optical properties, but with tailored thermal properties as well to manage waste heat. Indeed, one of the most prevalent and long-standing challenges in designing improved microelectronics is that of increasing power density and the dissipation of thermal hot spots in dense integrated
circuits [46, 47]. When material grain sizes are reduced to the order of phonon mean-free-paths (10’s-100’s of nanometers), thermal transport becomes largely ballistic and collisions with interfaces become the dominant phonon-scattering mechanism [48, 49]. Moreover, the grain resistance decreases as well since $R = \frac{L}{\kappa A}$, where $\kappa$ is the grain thermal conductivity. Therefore, the thermal resistance of interfaces between material grains becomes increasingly dominant in the overall thermal resistance of the device and can therefore become the main bottleneck for thermal management [50, 48]. Consequently, as devices have become smaller and more complex, there are a larger number of interfaces between heat source and sink leading researchers to turn their attention from high thermal conductivity materials toward the thermal resistance at interfaces [48, 49].

For vdW 2D materials, the issue of heat dissipation may be further complicated by the presence of vdW bonding in the cross-plane direction [51], which also governs the interface with surrounding 3D contacts [22]. Since 2D materials are in the limit of high surface-area-to-volume ratio, the role of interfaces is even more pertinent to reliable device performance. Consider a 2DFET where the 2D active-layer sits on an electrically insulating 3D substrate. The majority of heat generated in the active layer eventually travels across the 2D/3D interface and through the underlying substrate [52]. The former relies on the thermal boundary conductance (TBC) of the 2D/3D vdW interface, while the latter depends on the thickness of the substrate and its thermal conductivity. The thermal conductivity of the substrate is typically not as crucial as the TBC, because the substrate is often thin and potentially welded to a higher thermal conductivity material, as in the case of the ubiquitously used SiO$_2$/Si platform. This implies that the major impeding factor in the thermal management of 2D-based devices will be the TBC at their 2D/3D interfaces [52]. However, despite the important role of thermal boundary conductance in modern microelectronics, the amount of literature on the TBC of 2D/3D vdW interfaces pales in comparison to the number of studies on the electronic, mechanical, and optical properties of 2D materials.
Nonetheless, there have been several studies to experimentally measure 2D/3D vdW TBC using Raman spectroscopy [53, 54, 8, 55, 56], differential 3-ω [6, 7], pump-probe [57, 58, 59], time- and frequency-domain thermoreflectance (TDTR/FDTR) [60, 5, 61], and, more recently, electrical thermometry platforms [9, 52]. However, these studies focus mostly on a subset of 2D materials (i.e., graphene, BN, and select TMDs) and are spread across several works. As a result, there is often variation in the measured values for the same 2D/3D pairing due to differences in sample preparation/quality, different measurement techniques, and the presence (or absence) of encapsulation which is often limited by measurement technique. Further, experimental measurements obtain lumped-sum values that cannot be readily separated into their comprising parts without complimentary measurements, such as those with and without an encapsulating layer [9]. Therefore, there is a need for a theoretical framework from which a systematic investigation of 2D/3D vdW TBC for a wide-range of interface pairs can be performed.

Computational solid-state physics based on density functional theory and subsequent energy transport modeling has become commonplace in accompanying experimental studies to help eliminate measurement unknowns and provide insightful physical explanations. Further, computational models of higher complexity continue to be enabled by the advancement of high-performance computing (HPC) where advancements in simulation shrink the gap between idealized computer models and real-world systems. Moreover, the success of computational science and HPC clusters has led to the origin of a natural feedback loop, where computation aids in the design of better processing devices which in turn enables better simulation [62]. Altogether, this has led to a reinvigoration of basic material properties research where the integration of computational models with experimentation are making significant impacts in industries where plateaus in performance are stifling progress. In applications such as integrated circuits, energy storage, and renewable energy technologies (e.g., solar cells and thermoelectrics), there have been large leaps in performance and cost-efficiency owed to discoveries in fundamental material science.
In this dissertation, first-principles phonon dispersion calculations and the phonon Boltzmann transport equation are leveraged to systematically study phonon transport across 2D/3D interfaces. The motivation is the fundamental importance of interface thermal conductance in modern microelectronics and the apparent lack of literature on the TBC of 2D/3D interfaces. This work is computational in nature which lends itself to providing physical explanations and identifying trends across material systems. It is important to note the critical role of computational material science employed in areas where experimental measurements are novel and in need of refinement, such as in the case here of 2D/3D vdW thermal interface transport. By using a computational model, upper and lower bounds on interface thermal transport can be estimated and comprehensive analysis across different 2D/3D pairs can be performed more feasibly than experimental setups.

1.1 Outline of Dissertation

The remainder of the document is organized as follows: Chapter 2 introduces the relevant theoretical approaches that are traditionally used to study phonon interface transport. The limitations of these models in the context of 2D/3D interfaces are emphasized and then a new 2D/3D phonon interface model is introduced and then employed to study a wide range of 2D/3D interfaces over several studies. In Chapter 3, the thermal boundary conductance of 42 interfaces involving graphene, hBN, and four select transition metal dichalcogenides is calculated. Emphasis is given to the role of substrate material and trends in the TBC as a function of the overlap between vibrational spectra and constituent material properties. Chapter 4 then expands the model to include anharmonic effects (internal to the 2D layer) on the TBC, and interfaces of bare and encapsulated beyond-graphene 2D materials on SiO$_2$ and GaN are investigated. Chapter 5 employs machine learning on a further expanded dataset of 2D/3D vdW TBC and performs sensitivity analysis to identify key material descriptors important for making machine learning predictions. Finally, Chapter 6 investigates the TBC of multilayered and heterostructured vdW 2D materials on SiO$_2$. 
CHAPTER 2

METHODOLOGY

In this chapter, the methods central to this dissertation are introduced and discussed. Namely, the diffuse and acoustic mismatch models for 3D/3D (solid-solid) interface transport are briefly reviewed and their pitfalls for addressing 2D/3D interface transport are highlighted. A new formalism is then derived from the phonon Boltzmann transport equation (pBTE) which describes the unique physical mechanisms governing interface phonon transport at 2D/3D vdW interfaces. The Massachusetts Green High Performance Computing Center (MGHPCC) is used to accelerate phonon calculations that are performed with open-source \textit{ab-initio} softwares QUANTUM ESPRESSO [63] and Phonopy [64]. Phonon dispersion data is collected into a growing dataset of 2D and 3D materials which are then used as input data to the pBTE vdW 2D/3D model.

2.1 Phonon dispersion relation

The thermal analog to electronic band structure $E(\vec{k})$ is the phonon dispersion relation $\omega_j(\vec{q})$ which gives the normal modes of vibration of a crystal structure and can be used to further characterize its thermal properties [65, 64]. Phonons are treated as plane waves, and so the phonon dispersion relates a phonon frequency $\omega$ to its allowable phonon modes $\vec{q}$ and branch $j$. The phonon mode $\vec{q}$ describes the direction of propagation within the crystal lattice while the branch $j$ describes the type (or character) of atomic displacements that the propagating wave displays. For a unit cell with $N$ many atoms, there are $3N$ many phonon branches. The first three branches represent acoustic phonons and are responsible for transporting thermal energy. The remaining phonon branches represent optical phonons.
which mostly act as standing waves due to their low group velocity and therefore store thermal energy instead of contributing to transport [66]. This is the case for transport within the material as well as for interface transport [66, 67]. Exampled phonon dispersions are shown for face-center cubic silicon (black lines) and germanium (red lines) in Fig. 2.1a.

For 3D materials, the three acoustic branches are split into one longitudinal (LA) branch, where atoms are displaced along the direction of propagation, and two transverse (TA1 and TA2) branches, where atoms are displaced perpendicular to the direction of propagation.

For 2D materials, one of the transverse branches becomes the flexural (ZA) phonon branch that represents out-of-plane atomic displacements relative to the 2D-layers in-plane directions. In the long-wavelength limit, where $\lambda = \frac{2\pi}{q}$ is large (i.e., $|q| \rightarrow 0$), the flexural phonon branch of 2D materials has a unique quadratic dispersion $\omega_{ZA}(\vec{q}) \approx \alpha q^2$ [68, 69], which contrasts with the typical linear dispersion $\omega(\vec{q}) \approx c_s q$ seen in other acoustic phonons branches, where $c_s$ is the speed of sound.
Once the dispersion relation is computed from first-principles, the vibrational density of states (vDOS) of each material is then calculated. For either 2D or 3D materials, the vibrational density of states is solved as,

\[
D(j, \omega) = \int \delta[\omega - \omega_j(\vec{q})]d\vec{q}.
\]  

(2.1)

The Brillouin zone integration method of Gilat and Raubenheimer [70] can be used to solve the delta integral numerically. The total vDOS is obtained by summing over each branch contribution, \(D(\omega) = \sum_j D(j, \omega)\). The vDOS of all materials discussed in this work are computed from first-principles with the exception of select amorphous materials (\(\text{SiO}_2\), \(\text{AlO}_x\), and \(\text{HfO}_2\)) and polar crystals (\(\text{Al}_2\text{O}_3\)). Density functional theory simulations assume periodic boundary conditions and are limited in cases where symmetry is low, such as in the case of amorphous materials whose atomic positions have no long-range order. Hence, for amorphous \(\text{SiO}_2\), aluminum oxide \(\text{AlO}_x\), and hafnium oxide \(\text{HfO}_2\) related literature is relied upon and their vDOS are extracted from molecular dynamics (MD) [71, 72] and first-principles MD simulations [73]. For the polar material \(\text{Al}_2\text{O}_3\), Wang et al. [74] accurately calculated the full phonon dispersion and vDOS using a mixed-space approach that combines density functional perturbation theory and the frozen-phonon method. The vDOS for \(\text{Al}_2\text{O}_3\) is therefore extracted from their calculations.

2.2 Phonon transport across 3D/3D interfaces

When one side of an interface is non-metal, interface thermal transport is dominated by the phonon contribution [67]. Therefore, only the phonon part of interface thermal transport is considered in our formalism as well as in the methods discussed below. When two materials are in contact and form some atomic bonding at their interface, there will be a transfer of thermal energy from one material (Material 1 at temperature \(T_H\)) to the other (Material 2 at temperature \(T_C\)) provided that \(T_H > T_C\). In such a case, a phonon traveling
in Material 1 with wave vector \( \vec{q}_i \) (and branch \( j \)) that is incident on the interface can either reflect back (\( \vec{q}_r \)) into Material 1, transmit (\( \vec{q}_t \)) into Material 2, or some combination of the two (see Fig. 2.2a) [75, 76]. The net heat flux \( Q_{1\rightarrow2} \) from Material 1 to Material 2 can then be related to a transmission probability \( \alpha \), that represents the probability that a given phonon is reflected or transmitted, as,

\[
Q_{1\rightarrow2} = \frac{1}{2} \sum_j \int \hbar \omega N_0(\omega, T) |\vec{v}_1(j, \omega) \cdot \vec{n}| \alpha_{1\rightarrow2}(j, \omega) d\omega .
\]  

(2.2)

In the above, \( N_0 \) is the equilibrium Bose-Einstein distribution function \( N_0(\omega, T) = ... \) \[ exp \left( \frac{\hbar \omega}{k_B T} \right) - 1 \] \(^{-1}\), \( \vec{v}_1 \) is the phonon group velocity of the incident phonon, \( \vec{n} \) is the normal vector of the interface, and \( \alpha_{1\rightarrow2} \) is the frequency- and branch-dependent transmission probability. The interface conductance can then be determined as the ratio of the net heat flux \( Q_{1\rightarrow2} \) over the temperature difference at the interface \( \Delta T = T_H - T_C \),

\[
TBC(T) = \frac{Q_{1\rightarrow2}}{\Delta T} = \frac{1}{2} \sum_j \int \hbar \omega \frac{dN_0(\omega, T)}{dT} |\vec{v}_1(j, \omega) \cdot \vec{n}| \alpha_{1\rightarrow2}(j, \omega) D_1(j, \omega) d\omega .
\]  

(2.3)

Figure 2.2: Diagrams showing the two general pictures of phonon interface transport at 3D/3D interfaces. One showing a smooth interface (a) where collisions are specular and momentum can be conserved, and another showing a rough interface (b) that destroys the phonon momentum \( (p = \hbar q) \) upon striking the interface.
In the above, $D_1(\j, \omega)$ is the vDOS of Material 1. The integral in Eq. 2.3 can then be solved numerically provided the transmission probability $\alpha$ is known. The challenge therefore lies in formulating the transmission probability [75, 67].

To this end, there are two long-standing models for computing the transmission probability $\alpha$; the diffuse mismatch model [77, 75, 76] (DMM) and the acoustic mismatch model [78, 79] (AMM). For smooth interfaces the AMM is often used, where phonon transport across the interface is determined by the acoustic impedances of either medium in a manner akin to Snell’s Law. Under the AMM, phonons that strike the interface within a cone of incident angles are smaller than the critical angle have a specular transmission probability that can be written as,

$$\alpha_{1\to2(AMM)} = \frac{4z_1 z_2 \cos \theta_1 \cos \theta_2}{(z_1 \cos \theta_1 + z_2 \cos \theta_2)^2}. \quad (2.4)$$

Here $z_1$ and $z_2$ are the acoustic impedances between either material, $\theta_1$ and $\theta_2$ are the angles between the interface normal and phonon propagation in either material. This process is graphically depicted in Fig. 2.2a. The AMM works best at low-temperatures or when interface transport is dominated by long-wavelength phonons that are unaffected by interface asperities [67].

In the DMM, the interface is treated as completely diffuse where phonons impinging on the interface are destroyed and the probability of transmission or reflection is determined by the ratio of vibration density of states between the two materials. This is graphically seen in Fig. 2.2b where the incident phonon wave-vector $\vec{q}_i$ is destroyed at the interface. The transmission probability then takes the form,

$$\alpha_{1\to2(DMM)}(\j, \omega) = \frac{\sum_j v_2(\j, \omega)D_2(\j, \omega)}{\sum_j v_2(\j, \omega)D_2(\j, \omega) + \sum_j v_1(\j, \omega)D_1(\j, \omega)}. \quad (2.5)$$

In cases where small-wavelength phonons dominate transport, the DMM can give good approximations to the thermal conductance. However, it gives a transmission probability
of 0.5 for acoustically matched interfaces \((D_1 = D_2\) and \(v_1 = v_2\)). Therefore, it is typically thought of as a lower bound for well-matched interfaces, whereas the AMM can be often taken as an upper bound on interface thermal conductance. Either model seldom fits experimental measurements perfectly across all temperatures, but instead act as two extremes giving lower (DMM) and upper (AMM) bounds for the thermal boundary conductance [67]. Therefore, interface transport models beyond AMM/DMM have been developed to bridge the gaps between them by considering the specularity of incident phonons and better capturing the interplay between internal scattering, surface roughness, and acoustic mismatch between domains [67, 80].

### 2.2.1 Acoustic mismatch model for van der Waals interfaces

Further beyond the AMM, DMM, and models that interpolate between them, are interfaces that account for van der Waals bonding at the interface instead of covalent bonding. For such vdW interfaces, Prasher developed a variation of the AMM where a vdW coupling term is introduced [81]. In this approach the transmission coefficient from Eq. 2.4 gains a term in the denominator that is proportional to the vdW coupling \((K_a)\) at the interface,

\[
\alpha_{1\rightarrow2(\text{vdW+AMM})} = \frac{4z_1z_2\cos\theta_1\cos\theta_2}{(z_1\cos\theta_1 + z_2\cos\theta_2)^2 + \frac{\omega^2}{K_a^2}(z_1z_2\cos\theta_1\cos\theta_2)^2}.
\]

In the limit of a welded interface where \(K_a \rightarrow \infty\) the second term in the denominator vanishes, and we recover the AMM. On the other hand, when \(K_a\) is weak (large vdW gaps) the second term in the denominator dominates resulting in a quadratic dependence on spring coupling and phonon frequency \(\alpha_{(\text{vdW+AMM})} \propto K_a^2/\omega^2\) – which suggests that low-frequency, long-wavelength phonons are primary TBC heat carriers in the limit of weak \(K_a\). The vdW+AMM model has been successfully been applied to transferred silicon nanomembranes (3D/3D) interfaces involving a vdW gap [82].
2.2.2 Limitations of existing models

However, in the case of 2D-3D interface transport, neither the AMM, DMM, or the vdW+AMM can be employed. The reasoning within the AMM/vdW+AMM is that the acoustic impedance of the 2D material $z_1 \cos \theta_1 = \rho_1 v^\perp$ depends on the phonon velocity perpendicular to the interface. Since all phonons in the 2D layer propagate in-plane and parallel to the interface, there are no phonon modes with non-zero $v^\perp$, hence the AMM/vdW+AMM gives a transmission coefficient $\alpha_{1 \to 2}$ that is always 0. There are rare occasions where the vdW+AMM may work for 2D-2D interfaces as demonstrated in [51] where the authors investigated the thermal conduction properties of single and bundled boron nitride nanoribbons. However, it is important to note that the domains constructing the interface have the same phase space and that the $v^\perp$ is assumed to be some non-zero in-plane phonon velocity in order to ensure a non-zero acoustic impedance. Within the DMM, whose $\alpha_{1 \to 2}$ yet again depends on the phonon velocity, the depiction of phonons impinging on the interface breaks down.

2.3 Phonon transport across 2D/3D vdW interfaces

In the case of 2D/3D vdW interfaces, instead of acoustic phonons striking the interface, flexural acoustic (ZA) phonons couple strongly with vibrational modes of the substrate by displacing atoms of the 2D-layer vertically which stretch or compress the van der Waals bonds at the interface. Since ZA phonons uniquely displace atoms out-of-plane (or parallel to the interface normal), they are the primary carriers of thermal energy across the interface [83]. Conversely, longitudinal and transverse acoustic phonons in the 2D-layer do not contribute directly to interface transport due to their in-plane atomic displacements which do not significantly affect the vdW bonding at the interface [84, 10, 9]. The interactions between flexural phonons in the 2D-layer and substrate vibrations are treated as a perturbation of the in-plane flexural wave wherein the energy $E = \hbar \omega$ of the in-plane wave is transferred to the substrate [4]. The substrate scattering rate is obtained through Fermi’s Golden Rule.
Figure 2.3: A schematic of a single-layer black phosphorene 2D FET is shown in (a). A diagram of the relevant scattering mechanisms and direction of heat from source to sink is shown in (b). This figure is adapted from Ref. [3].

[84] in the next section. The transfer from ZA phonon to substrate vibrational mode is elastic and does not conserve momentum due to the mismatch between phase spaces and the presence of atomic-scale roughness at the substrate surface which randomizes the phonon momentum. A further effect of phonon scattering with the substrate is that the ZA phonon population is depopulated resulting in a decrease in the temperature of the ZA phonon population. There is then a non-equilibrium condition between ZA phonons at temperature $T_{ZA} > T_{sub}$ (where $T_{sub}$ is the temperature of the substrate) and other thermal sources in the 2D-layer at a steady-state temperature $T_H > T_{ZA}$. Flexural phonons are replenished by internal scattering mechanisms [3] which may include scattering with electrons, other phonons (LA, TA, and optical), and an encapsulating layer. The general flow of thermal energy from hot electron injection to the substrate is graphically shown in Fig. 2.3a and further explained schematically in Fig. 2.3b.

The steady-state phonon Boltzmann transport equation (pBTE) for ZA phonons within the relaxation time approximation (RTA) [85] is,

$$\bar{v}_{ZA}(\vec{q}) \cdot \nabla_T \frac{N_0(\omega, T)}{dT} = - \frac{N_{ZA}(\vec{q}) - N_0(\omega, T)}{\tau(\omega)}. \quad (2.7)$$
$N_{ZA}(\vec{q})$ is the out-of-equilibrium ZA phonon distribution function, $N_0$ is the Bose-Einstein distribution, $\tau^{-1}(\omega)$ is the total scattering rate, and $\vec{v}_{ZA}$ and $\omega$ are the phonon group velocity and angular frequency of ZA phonons, respectively. Since the 2D-layer and the substrate are at different temperatures, the total scattering rate $\Gamma = \tau^{-1}$ can be separated into two parts; one capturing the interactions of ZA phonons with other heat sources (termed $\Gamma_{int}$) at $T_H$ and the other capturing ZA phonon interactions with the substrate (termed $\Gamma_{sub}$) at $T_{sub}$, where it is assumed $T_{sub} < T_H$. The pBTE then expands into

$$\vec{v}_{ZA}(\vec{q}) \cdot \nabla T \frac{N_0(\omega, T)}{dT} = -\Gamma_{sub}(\omega) [N_{ZA}(\vec{q}) - N_0(\omega, T_{sub})]$$
$$-\Gamma_{int}(\omega, T_H) [N_{ZA}(\vec{q}) - N_0(\omega, T_H)] , \quad (2.8)$$

where $\Gamma_{int}$ is the internal scattering rate of the 2D-layer driving the out-of-equilibrium ZA phonons distribution $N_{ZA}$ to an equilibrium distribution at $T_H$. Then, $\Gamma_{sub}$ is the substrate scattering rate driving $N_{ZA}$ to an equilibrium distribution at $T_{sub}$.

Assuming uniform heating across the 2D-layer, the LHS of Eq. 2.8 can be made zero and the out-of-equilibrium distribution $N_{ZA}$ can be found as,

$$N_{ZA}(\vec{q}) = \frac{\Gamma_{sub}(\omega) N_0(\omega, T_{sub}) + \Gamma_{int}(\omega, T_H) N_0(\omega, T_H)}{\Gamma_{sub}(\omega) + \Gamma_{int}(\omega, T_H)} . \quad (2.9)$$

From here, the net heat flux into the substrate can be solved by integrating over the frequency spectrum,

$$Q = \int \hbar \omega N_{ZA}(\vec{q}) D_{2D}(\omega) d\omega , \quad (2.10)$$

where $D_{2D}(\omega)$ is the vDOS of flexural phonons. Substituting $N_{ZA}$ into the heat flux $Q$ and expanding for a small temperature gradient $\Delta T = T_H - T_{sub}$ between the 2D-layer and the substrate, the TBC for a single-layer 2D/3D interface is obtained as

$$TBC(T) = \frac{Q}{\Delta T} = \int \hbar \omega(\vec{q}) \frac{dN_0(\omega, T)}{dT} \frac{\Gamma_{sub}(\omega)}{\Gamma_{sub}(\omega) + \Gamma_{int}(\omega, T)} D_{2D}(\omega) d\omega . \quad (2.11)$$
This formula is the same as Eq. 2.3 [77, 67], except the transmission coefficient $\alpha$, has now become a function of the independent scattering mechanisms acting on ZA phonons. Further, compared to Eq. 2.3 there is no $|\vec{v}_1(j, \omega) \cdot \vec{n}|$ term either as all ZA phonons have propagating velocities that are parallel to the interface (perpendicular to the surface normal), and thus this term would trivially be zero. The $\Gamma_{\text{sub}}\Gamma_{\text{int}}/\left[\Gamma_{\text{sub}} + \Gamma_{\text{int}}\right]$ term in Eq. 2.11 is referred to as the effective substrate scattering rate $\Gamma_{\text{eff}}$ (illustrated in Fig. 2.3b) and is equivalent to two conductors in series: one representing internal heat transfer from internal degrees of freedom (LA/TA phonons, electrons, etc.) to ZA phonons and the other external heat transfer from ZA phonons to the substrate. The resistance associated with the substrate scattering rate $\Gamma_{\text{sub}}$ is denoted as the external resistance and the additional resistance caused by weak internal scattering $\Gamma_{\text{int}}$ as the internal resistance.

2.3.1 Flexural phonon scattering with substrate modes

Fermi’s Golden rule is employed to capture the scattering rate between flexural phonons and substrate vibrational modes at the interface and is written as,

$$\Gamma(q) = \frac{2\pi}{\hbar} \sum_{q_f} \left| \langle u_f | H_{\text{ph}}^f | u_i \rangle \right|^2 \delta(E_f - E_i)$$

(2.12)

where $u_{i,f}$ and $E_{i,f} = \hbar \omega_{i,f}$ represent the phonon displacements and energies of initial and final states, respectively, and $H_{\text{ph}}^f$ is the perturbation Hamiltonian. Since the perturbations are acting on flexural waves we can write $H_{\text{ph}}^f$ as a first-order expansion in the phonon frequency as $H_{\text{ph}}^f = K_a \frac{d\omega}{dK_a}$. Taking the flexural branch of a substrate supported single 2D-layer to be $\tilde{\omega}_{ZA}(q) = \sqrt{\omega_{ZA}^2(q) + \frac{K_a}{m_{2D}}} \left(\text{obtained below in Section 2.3.3}\right)$, we find that $K_a \frac{\partial \tilde{\omega}}{\partial K_a} = \frac{K_a}{2m_{2D}}$. Since $H_{\text{ph}}^f$ is not dependent on the displacements $u_{i,f}$, it can be taken out of the inner product $\left| \langle u_f | H_{\text{ph}}^f | u_i \rangle \right|^2$ and Eq. 2.12 can be written as,

$$\Gamma(q) = \frac{2\pi}{\hbar} (H_{\text{ph}}^f)^2 \sum_{q_f} |\langle u_f | u_i \rangle|^2 \delta(E_f - E_i).$$

(2.13)
Recognizing that \( \sum_{q_i} |\langle u_f | u_i \rangle|^2 = \frac{1}{3} \), that \( \sum_{q_i} \delta(E_f - E_i) = \hbar \sum_{q_i} \delta(\omega_f - \omega_i) \) is the density of final states (i.e., the substrate vDOS \( D_{3D} \)), and substituting in for \( H_{ph}^f \), the above becomes,

\[
\Gamma(\omega) = \frac{2\pi}{3} \left( \frac{K_a}{2m_\omega} \right)^2 D_{3D}(\omega). 
\] (2.14)

Rearranging terms and normalizing the substrate vDOS to \( \int D_{\text{sub}}(\omega)d\omega = 3 \), accounting for 3 acoustic phonon branches that carry transferred heat away from the interface, we arrive at the substrate scattering rate,

\[
\Gamma_{\text{sub}}(\omega) = \frac{\pi}{2} \frac{D_{3D}(\omega)}{m_{2D}m_{\text{sub}}} \frac{K_a^2}{\omega^2}. 
\] (2.15)

where \( D_{3D}(\omega) \) is the substrate (3D) vDOS, \( m_{2D} \) and \( m_{\text{sub}} \) are the atomic masses in contact at the interface of the 2D-material and substrate, and \( \omega \) is the phonon vibrational frequency. A similar derivation can be found in the supporting information of Ref. [84]. For a given substrate, \( \Gamma_{\text{sub}}(\omega) \) is proportional to \( 1/\omega^2 \) and is independent of temperature. The \( 1/\omega^2 \) dependence suggests, similar to the vdW+AMM (Eq. 2.6), that the majority of phonon transfer across the interface comes from long-wavelength, low-energy phonons with q-vectors close to the Brillouin zone center. This is central to the analysis discussed in Chapters 3 and 4 where it is shown that the low-energy features in the vDOS of both materials are used to explain trends seen across different 2D/3D pairings.

The vdW spring coupling constant is proportional to the adhesion energy [86] between the 2D layer and substrate which is generally difficult to quantify experimentally [81] for 2D/3D interfaces. An upper bound for \( K_a \) can be roughly determined as the vdW interlayer coupling of the bulk counterpart of the 2D material which can be as high as 8 N.m\(^{-1}\) in MoS\(_2\) and WSe\(_2\) [87]. This is based on the assumption that the vdW interlayer coupling in the bulk-vdW material is inherently stronger than the coupling between the 2D layer and a dissimilar substrate. As for computing the vdW coupling strength between a 2D material
and substrate, Ong et al. [10] used DFT to calculate $K_a$ for Gr/SiO$_2$ and MoS$_2$/SiO$_2$ interfaces with H and OH substrate surface termination atoms. There, values of $K_a$ for H (or, OH) termination were reported to be 8.18 (6.45) N.m$^{-1}$ and 2.36 (4.27) N.m$^{-1}$ for Gr/SiO$_2$ and MoS$_2$/SiO$_2$, respectively. In both Chapters 3 and 4, assumptions on the value $K_a$ are made as a means to an end in the absence of further data on a particular interface pairing. In some cases, experimental measurements are used to arrive at a value of $K_a$, and further extrapolations are made therein. It is worth noting that the values of $K_a$ extracted from experimentally measured TBC values are lower than those reported for bulk interlayer vdW coupling and DFT-calculated values which lends to the validity of this model [9, 88, 55].

### 2.3.2 Internal scattering of flexural phonons

In modeling the internal scattering mechanisms that repopulate the ZA phonon population to facilitate interface transport, consideration is given to anharmonic three-phonon (normal and umklapp) scattering – $\Gamma_{an} = \Gamma_N + \Gamma_U$ – and scattering with an encapsulating layer when one is present. The frequency- and temperature-dependent normal and umklapp three-phonon scattering rates ($\Gamma_N$ and $\Gamma_U$) are computed following the empirical formalism presented by Morelli et al. [89], which has adapted to 2D materials [85] where good agreement with measured thermal conductivity of graphene was found. In this formalism, $1/\tau_Q^N = B_N \omega_Q^{a_N} T^{b_N} e^{-\Theta_j/3T}$ and $1/\tau_Q^U = B_U \omega_Q^{a_U} T^{b_U} e^{-\Theta_j/3T}$, where the prefactor terms $B_N$ and $B_U$ are written as

$$B_N(a_N, b_N) = \left( \frac{k_B}{\hbar} \right)^{b_N} \frac{\hbar \gamma_j^{2[S_0h_{2D}]}(a_n+b_N-2)/3}{m_{2D}^2 \Theta_j^{b_N} + b_N}, \quad (2.16)$$

and

$$B_U(a_U, b_U) = \frac{\hbar \gamma_j^2}{m_{2D}^2 \Theta_j^{b_U}}, \quad (2.17)$$

respectively. In the above equations, $\Theta_j$ is the branch-wise Debye temperature, $\gamma_j$ is the branch-wise Grüneisen parameter, $S_0$ is the surface area of the 2D layer unit cell ($S_0 =$
\( \sqrt{2} a_0 \), and \( m_{2D} \) is the unit cell atomic mass. The empirical exponential factors \( a_N, b_N, a_U, \) and \( b_U \) that determine the frequency and temperature dependencies for normal and umklapp scattering are \( a_N = [1 2 2], b_N = 1, a_U = 2, \) and \( b_U = 1, \) respectively. For high thermal conductivity 2D materials that have a large ZA branch contribution, internal scattering could be quite weak leading to a thermal bottleneck caused by slow repopulation of ZA phonons.

In many cases, 2D materials are encapsulated to prevent degradation from atmospheric effects such as oxidation [90, 91]. Encapsulating layers increase the internal scattering of flexural phonons and can therefore reduce the internal resistance part of TBC and potentially increase the effective heat transfer to the substrate [88]. ZA phonon interactions with an encapsulating layer are analogous to those with the substrate, however, in this case the 2D layer and the coating layer are thermally equilibrated at steady-state. As a result, the scattering rate for an encapsulating layer must satisfy the principle of detailed balance and takes the form,

\[
\Gamma_{\text{enc}}(\omega) = \frac{\pi}{2} K_{\text{enc}}^2 \frac{D_{\text{enc}}(\omega)}{m_{\text{enc}}} + \frac{D_{2D}(\omega)}{m_{2D}} \frac{1}{\omega^2},
\]

where \( K_{\text{enc}} \) is the vdW coupling between the 2D-layer and encapsulation, \( D_{\text{enc}}(\omega) \) is the vDOS of the encapsulating layer, and \( m_{\text{enc}} \) is the mass of the surface atoms of the encapsulating layer. Altogether, the internal scattering rate acting to replenish ZA phonons can be written as the sum of independent mechanisms, \( \Gamma_{\text{int}} = \Gamma_{\text{anh}} + \Gamma_{\text{enc}}. \)

### 2.3.3 Substrate and multilayer effects on flexural vibrations

When a single-layered 2D material couples to a substrate and then subsequently to additional 2D-layers, the flexural vibrational modes are affected by the additional coupling forces between the materials. When considering just \( \Gamma \)-point vibrations, Luo et al. [92] used a simple linear chain model (LCM) (see Fig. 2.4) to approximate the vibrational modes of epitaxial thin films comprised of select metals (Na, Cu, Pb, etc.). Few-layer
2D/3D systems are equivalent to the epitaxial thin films by replacing the interlayer coupling constants with weaker van der Waals spring constants. The equations of motion for an N-layer 2D stack on a substrate are written as [93],

\[(\rho\omega^2 - \kappa q^4)u_1 = g(u_1 - u_2)\], \hspace{1cm} (2.19)

\[(\rho\omega^2 - \kappa q^4)u_N = g(u_N - u_{N-1})\], \hspace{1cm} (2.20)

\[(\rho\omega^2 - \kappa q^4)u_j = g(2u_j - u_{j+1} - u_{j-1})\], \hspace{1cm} (2.21)

where \(\kappa q^4\) is the square of the analytical expression for zone-center flexural phonons \((\omega_{ZA}(q))^2 \approx \kappa q^4\), \(\rho\) is the mass density, \(g\) is the vdW spring coupling per unit area, and \(u_j\) is the atomic displacement for layer \(j\). The notation of Eqs. 2.19-2.21 is the same as in the Appendix of Ref. [93] except the imaginary term containing the flexural phonon damping function \(\gamma\) is assumed to be zero here. This system of equations can be written more compactly as,

\[\sum_{j=1}^{N} (V_{ij} - z\delta_{ij})u_j = 0\], \hspace{1cm} (2.22)

where \(z(q, \omega) = \rho\omega - \kappa q^4\) and \(V_{ij} = g(\delta_{i,j-1} + \delta_{i,j+1})\) for \(i \neq j\). Assuming non-zero displacements \(u_j\) and considering a single 2D-layer on a substrate we have the condition that \((V_{ij} - z\delta_{ij}) = 0\) which can be written as \((\rho\omega^2 - \kappa q^4 - g) = 0\). Solving for \(\omega\) one obtains,

\[\omega = \sqrt{\frac{g}{\rho} + \frac{\kappa}{\rho} q^4}.\] \hspace{1cm} (2.23)

The analytical expression of zone-center flexural phonons can then be replaced with its full q-dependent dispersion calculated from first-principles to obtain, \(\omega = \sqrt{\omega_{ZA}^2(q) + \frac{g}{\rho}}\)

where \(\frac{g}{\rho}\) is equivalent to \(\frac{K_a}{m_{2D}}\) since \(g = K_a/S_{2D}\) and \(\rho = m_{2D}/S_{2D}\) and so a term of 2D unit cell area cancels. This term is referred to as the resonant flexural frequency gap.
$\omega_0^2 = \frac{g}{\rho}$. Flexural phonon frequencies of single-layer 2D/3D interfaces are then modified according to $\tilde{\omega}_{ZA}(\vec{q}) = \sqrt{\omega_{ZA}^2(\vec{q}) + \omega_0^2}$, where $\omega_{ZA}$ is the as-calculated frequencies and $\omega_0$ is the gapping frequency and takes values of $\omega_0 = \sqrt{K_a/m_{2D}}$ [94, 86]. Examples of the gapping effect on the dispersion and vDOS of 2D materials can be seen in Fig. 3.1 and 3.3, respectively. The amount of resonant gapping is important towards shaping the low-energy vDOS of the 2D material, which as previously mentioned, is the region where most interface transport is occurring. The methods discussed up to here are sufficient for Chapters 3 to 5 which are concerned with computing the TBC for single-layered bare and encapsulated 2D/3D interfaces.

Upon adding 2D layers, the phonon dispersion of the few-layer structure is further modified, gaining additional branches representing various flexural modes brought on by the larger Brillouin zone of the heterostructured material. Solving the system of equations above where the mass and springs are the same (see Fig. 2.4a), one arrives at a similar analytical expression for the flexural phonons of the few-layer 2D system [93],

Figure 2.4: The linear chain model for a van der Waals 2D system comprised of the same material (a) and mixed heterostructure (b) is shown.
\[ \tilde{\omega}^j_{ZA}(\vec{q}) = \sqrt{\omega^2_{ZA}(\vec{q}) + \omega_0^2 + \frac{2K_z}{m_{2D}} \sin^2 \left( \frac{(i-1)\pi}{N} \right),} \]  

(2.24)

where \( \omega_{ZA} \) is the as-calculated ZA phonon dispersion, \( K_z \) is the vdW spring coupling between 2D layers, and \( N \) is the total number of 2D layers in the stack. For a van der Waals heterostructure where the masses and springs may be different for each layer (see Fig. 2.4b), there is no analytical expression for the linear chain of atoms. Therefore, we construct the dynamical matrix described by Eqs. 2.19-2.21, inputting layer specific properties for \( \rho \), \( g \), and \( \omega_{ZA} \), and numerically solve for the phonon frequencies and displacements. We then employ this model to predict the TBC for few-layered and vdW heterostructured 2D/3D systems in Chapter 6.

### 2.3.4 Multilayer 2D/3D thermal boundary conductance

The phonon density of states of the few-layered 2D stack is then computed in a similar manner as previous sections. Eqs. 2.11, 2.15, and 2.18 are modified to account for contributions from the additional branches of the few-layered systems, and are written as,

\[
\Gamma_{i,\text{sub}}(\omega) = \frac{\pi}{2} \left[ \frac{m_{1,2D}}{K_a} + \frac{(i-1)m_{i,2D}}{K_{i,z}} \right]^{-2} \frac{m_{1,2D}}{m_{\text{sub}}} \frac{D_{\text{sub}}(\omega)}{\omega^2},
\]  

(2.25)

\[
\Gamma_{i,\text{enc}}(\omega) = \frac{\pi}{2} \left[ \frac{m_{N,2D}}{K_{\text{enc}}} + \frac{(N-i)m_{N-i,2D}}{K_{i,z}} \right]^{-2} \ldots
\]  

\[
\times m_{N,2D} \left[ \frac{D_{\text{enc}}(\omega)}{m_{\text{enc}}} + \frac{D_{N-i,2D}(\omega)}{m_{N-i,2D}} \right] \frac{1}{\omega^2},
\]  

(2.26)

\[
TBC_i(T) = \int \hbar \omega \frac{dN_0(T)}{dT} \frac{\Gamma_{i,\text{sub}}(\omega)}{\Gamma_{i,\text{sub}}(\omega) + \Gamma_{i,\text{int}}(\omega, T)} \frac{\Gamma_{i,\text{int}}(\omega, T)}{D_{i,2D}(\omega)} d\omega,
\]  

(2.27)

where \( \Gamma_{i,\text{int}} \) includes the branch-wise scattering rate with the encapsulating layer (\( \Gamma_{i,\text{enc}} \)) – the same as the definition under Eq. 2.18. \( K_{\text{enc}}, m_{\text{enc}}, \) and \( D_{\text{enc}} \) represent the vdW spring coupling constant, atomic mass, and phonon density of states of the encapsulating layer. \( m_{i,2D} \) represents the unit cell mass of the \( i^{th} \) 2D layer.
CHAPTER 3

QUANTIFYING THERMAL BOUNDARY CONDUCTANCE OF 2D-3D INTERFACES

In this chapter, the TBC of 42 2D/3D vdW interfaces is computed using the model described in the previous chapter. The TBC computed here represents the external TBC and does not include the effects of internal scattering on flexural phonons. This enables a careful analysis on the impact of the substrate vDOS on the TBC. With respect to $\Gamma_{eff}$, this is equivalent to implying that internal scattering via $\Gamma_{int} \gg \Gamma_{sub}$ is sufficiently large such that the corresponding internal resistance is very small in comparison to the resistance with the substrate. The TBC is computed for interfaces involving Gr, BN, MX$_2$ TMDs (where M=Mo,W and X=S,Se) for 2D materials and SiO$_2$, AlO$_x$, GaN, AlN, 6H-SiC, sapphire (Al$_2$O$_3$), and diamond as (3D) substrates. The phonon dispersion for graphene, hBN, MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$ is shown in Fig. 3.1. The gapped-ZA branch is shown in red, and the remaining branches in black. Similar to the earlier example of Si and Ge, one can see some fundamental rules-of-thumb about the phonon dispersion by comparing across these materials in Fig. 3.1. Namely, graphene and hBN have the same crystal structure and atomic mass, but the ZA phonon branch differs significantly due to the presence of two atomic masses in the hBN unit cell. Further, the four TMDs have the same crystal structure, but when the heavier W or Se atoms are swapped in for Mo or S the phonon dispersion becomes flatter.

3.1 Role of substrate: crystalline vs. amorphous

In Figure 3.2 the temperature dependence of the 42 pairs of 2D-substrate interfaces is shown. Our results show that the TBC can vary by nearly two orders of magnitude from as
Figure 3.1: The full phonon dispersion of graphene (a), h-BN (b), MoS$_2$ (c), MoSe$_2$ (d), WS$_2$ (e), and WSe$_2$ (f), calculated from first-principles using density functional perturbation theory. The gapped ZA (g-ZA) branch of each 2D layer is highlighted in red. This figure is adapted from Ref. [4].

low as $\approx 0.6 \text{ MW.m}^{-2}.\text{K}^{-1}$ (h-BN on diamond) to $\approx 40 \text{ MW.m}^{-2}.\text{K}^{-1}$ (hBN on SiO$_2$) for the same 2D layer by changing only the substrate material. The same coupling constant of $K_a = 2.7 \text{ N.m}^{-1}$ is used throughout to highlight the influence of constituent material properties such as vDOS and atomic mass on the TBC. The value of 2.7 N.m$^{-1}$ is extracted from experimental measurements [9] of TBC for Ti/Au/Gr/SiO$_2$ and Au/Ti/MoS$_2$/SiO$_2$ where $K_a$ is used as a fitting parameter. The extracted values of $K_a$ were lower than DFT-reported values for Gr/SiO$_2$ but roughly agreeing with MoS$_2$/SiO$_2$ interfaces [10]. It is noted that, although amorphous substrates can have rougher surface features than crystalline ones, rougher substrate surfaces may not necessarily lead to lower adhesion or vdW coupling. It was shown that some surface roughness can actually improve interface adhesion [95] and
Figure 3.2: Temperature dependence of the thermal boundary conductance (TBC) between our six 2D materials and substrates, exhibiting a roughly cubic trend at low temperatures, followed by saturation near room temperature, approximately following the heat capacity. The vdW coupling strength $K_a = 2.7 \text{ N.m}^{-1}$ is kept uniformly across all combinations to facilitate comparisons. Amorphous SiO$_2$ displays the highest TBC amongst all 2D-layers while diamond and crystalline Al$_2$O$_3$ display the lowest. This figure is adapted from Ref. [4].

for highly-flexible 2D materials, such as graphene, the 2D-layer can conform to the rough features of the substrate [84, 95].

The temperature dependence of the TBC follows roughly that of the heat capacity of the 2D material, increasing as $T^3$ at low temperatures and then saturating before reaching the Debye temperature $\Theta_{2D}$ of the 2D-material’s ZA branch where its heat capacity becomes constant [4]. However, graphene on diamond and Al$_2$O$_3$ shows a stronger T-dependence due to their high Debye temperatures. When compared to the crystalline substrates, atomic layers atop amorphous SiO$_2$ and AlO$_x$ have the highest TBC for all 2D materials, analogous to English et al. [96], who observed higher TBC at disordered 3D-3D interfaces. This observation was extended to graphene interfaces with MD simulations [97] by comparing the TBCs of graphene on crystalline and amorphous silicon carbides. It is demonstrated
Figure 3.3: The vibrational density of states (vDOS) of SiO$_2$ (a), GaN (b), AlN (c), SiC (d), crystalline Al$_2$O$_3$ (e), amorphous Al$_2$O$_3$ (e), and diamond (f) compared to the vDOS of their respective Debye model approximations (where applicable) as well as the vDOS of the ZA branch of graphene and MoS$_2$. This figure is adapted from Ref. [4].

Figure 3.3 shows the vDOS of each substrate (black lines) along with the vDOS of the out-of-plane flexural branch of graphene (solid red) and MoS$_2$ (dotted red). We note here that the large low-frequency peak in the vDOS of amorphous SiO$_2$ (Figure 3.3a) and AlO$_x$ (Figure 3.3e) leads to a large substrate scattering rate $\Gamma_{sub}(\omega) \propto D_{3D}(\omega)/\omega^2$; consequently, phonon modes with energies near the ZA gap $\omega_0$ contribute most to TBC [83].
The randomized atomic positions characteristic of amorphous materials destroy long-range order, and with it the higher frequency modes that comprise the van Hove singularities in crystalline materials are redistributed to lower frequencies [98, 99]. This redistribution causes the vDOS of amorphous materials to deviate significantly from the $\omega^2$ dependence, typical of crystalline solids at low frequencies; in contrast, the reduced vDOS $D_{3D}(\omega)/\omega^2$ of amorphous materials exhibits a low-frequency peak that is often termed the boson peak [100, 101]. The presence and location of the boson peak is identified as the cause of higher TBC. The peak for SiO$_2$ occurs around 10 meV whereas the peak for Al$_2$O$_3$ occurs around 20 meV, and as a result we see slightly larger TBC for most interfaces with SiO$_2$ as the substrate.

For crystalline substrates, we can again look at the vDOS at low-energies ($< 60$ meV), as shown in Figure 3.3, where the vDOS follows $D_{\text{Debye}} \approx \omega^2/v_{\text{sub}}^3$ until the acoustic branches deviate from their linearity and flatten near the Brillouin zone edge, forming van Hove singularities in the vDOS. We can see the inverse relationship of TBC on the substrate sound velocity as GaN, which has low acoustic sound velocity ($\sim 3200$ m/s), has the highest TBC among the crystalline materials. When we replace GaN with AlN and SiC the substrate sound velocity increases ($\sim 4800$ m/s and $\sim 5400$ m/s, respectively) and we see a decrease in the low-energy vDOS leading to a decrease in the TBC. The worst substrate for TBC is diamond, whose high sound velocity ($\sim 9500$ m/s) leads to minimal low-energy vDOS and a very low TBC.

### 3.2 Significance of Boson peak location in amorphous materials

To further elucidate the effects of the Boson peak location, we model a generalized amorphous substrate vDOS that follows a Lorentzian squared function for the Boson peak curve [102]

$$D_{BP}(\omega) = \frac{\omega^3}{(\omega^2 - v_0^2)^2},$$  \hspace{0.5cm} (3.1)
where \( v_0 \) roughly determines where the Boson peak occurs in the energy spectrum. We denote the precise location of the Boson peak for this Lorentzian squared function as \( \omega_{BP} = \sqrt{3} v_0 \). For comparison, we plot the vDOS of amorphous SiO\(_2\) and AlO\(_x\) alongside this generalized vDOS (\( D_{BP} \)) for several values of \( \omega_{BP} \) in Figure 3.4a. In Figure 3.4b we show the TBC between several 2D-layers and the generalized Boson Peak vDOS as a function of the Boson peak location \( \omega_{BP} \). We see a distinct peak around 4-6 meV which then drops rapidly thereafter. This indicates that substrates whose Boson peak occurs lower in the energy spectrum (roughly between 4-6 meV) will boost the TBC. Further, we see that softer 2D materials, such as the transition metal dichalcogenides (TMDs), respond better to this trend as their TBC peaks at a higher value than graphene. This highlights that the role of overlap between the vDOS of the 2D-layer and substrate is dominant over the increase of mass of the 2D-material atoms. Most interestingly, hBN atop this generalized substrate shows a peak around 600 MW.m\(^{-2}\).K\(^{-1}\) which far exceeds previously reported TBC values for 2D-oxide and 2D-semiconductor interfaces (both experimentally and theoretically) and

Figure 3.4: The vibrational density of states of amorphous SiO\(_2\) (solid black) and AlO\(_x\) (dotted black) shown in (a) alongside a Boson peak model at different values of \( v_0 \). The thermal boundary conductance between our six 2D-layers and a generalized amorphous substrate with a Boson peak vDOS is plotted as a function of the Boson peak location in (b). This figure is adapted from Ref. [4].
is within the range of TBC for graphene-metal [103, 104], 3D-3D vdW [82] and other 3D-3D covalently-bonded interfaces [105, 106].

The superior TBC of hBN on amorphous substrates over other 2D materials can be explained by its lower atomic mass, which maximizes the substrate scattering rate, in combination with its softer ZA phonon dispersion as compared to graphene (see Figure 3.1a and 3.1b). In hBN, the difference in masses of B and N atoms causes a gap between ZA and ZO phonons at the K point and a flattening of the phonon dispersion of ZA phonons along the M-K path [107]. The flatter dispersion leads to a larger vDOS at low-energies (0-30 meV) that combines with the larger substrate scattering rate, caused by the light monolayer mass and large substrate vDOS of amorphous materials, and maximizes the integrand of Eq. 2.11, ultimately boosting the TBC. We suspect that hBAs, having even larger mass difference and a flatter ZA branch [31], would exhibit even higher TBC on amorphous substrates.

3.3 Analytical expression of TBC for 2D-crystalline interfaces

Since most of the energy transfer is occurring at low-energies, and the low-energy vDOS of crystalline materials closely follows the Debye approximation, analytical expressions for the TBC can be derived by replacing the full substrate vDOS with the Debye approximation. Since \( \Gamma_{\text{int}} \gg \Gamma_{\text{sub}} \), Eq. 2.11 is written as,

\[
G_{\text{sub}}(T) = \int C_{2D}(\omega, T)D_{2D}(\omega)\Gamma_{\text{sub}}(\omega)d\omega ,
\]

where the substrate scattering rate is written as (same as Eq. 2.15),

\[
\Gamma_{\text{sub}}(\omega) = \frac{\pi}{2} \frac{D_{3D}(\omega)}{m_{\text{sub}}m_{2D}} \frac{K_a^2}{\omega^2} .
\]

If we assume the phonon dispersion in the substrate is linear with a speed of sound \( v_{\text{sub}} \), then the DOS \( D_{3D}(\omega) \) can be well approximated by the Debye model as,
Combining this DOS with Eq. (3.3), we cancel out the $\omega^2$ term and a power of $\pi$ to arrive at,

$$
\Gamma_{\text{sub}} = \left[ \frac{\pi}{2} \frac{K_a^2}{\omega^2 m_{\text{sub}} m_{2D}} \right] \left[ 3 \frac{\omega^2}{2\pi^2 v_{3\text{sub}}^3} \right] = \frac{3}{4\pi} \frac{K_a^2}{m_{\text{sub}} m_{2D} v_{3\text{sub}}^3}.
$$

(3.5)

We can now combine this $\Gamma_{\text{sub}}(\omega)$ with Eq. (3.2), factor out terms that are not $\omega$-dependent, and perform the integral over the phonon spectrum. After integrating the specific heat over the frequency range, we get the following,

$$
G_{\text{sub}}(T) = \frac{3}{4\pi} \frac{K_a^2}{m_{\text{sub}} m_{2D} v_{3\text{sub}}^3} C_{\text{2D}}(T),
$$

(3.6)

where $C_{\text{2D}}(T)$ is the heat capacity of the 2D material.

It is typical to normalize the $D(\omega)$ such that the total density of modes equals the atomic density

$$
\int_0^{\omega_D} 3 \frac{\omega^2}{2\pi^2 v_{3\text{sub}}^3} d\omega = \frac{3N}{V}.
$$

(3.7)

Solving the definite integral for the Debye frequency $\omega_D$ we obtain,

$$
\omega_D = \left( \frac{6\pi^2 v_{3\text{sub}}^3 N}{V} \right)^{1/3}.
$$

(3.8)

Introducing this vDOS into Eq. (3.3) and then replacing the resulting $\Gamma_{\text{sub}}$ in Eq. (3.6) we arrive at,

$$
G_{\text{sub}}(T) = \frac{3\pi}{2} \frac{K_a^2}{m_{\text{sub}} m_{2D} \omega_D^3} \frac{1}{\omega_D^3} C_{\text{2D}}(T).
$$

(3.9)
However, recalling Eq. (3.8) and examining the product of $m_{\text{sub}}\omega_D^3$, it can be recognized that

$$m_{\text{sub}}\omega_D^3 = \frac{6\pi^2 v_{\text{sub}}^3 m_{\text{sub}} N}{V} = 6\pi^2 v_{\text{sub}}^3 \rho_{\text{sub}}$$

with $\rho_{\text{sub}} = m_{\text{sub}} N / V$. Then Eq. (3.9) can be simplified further to

$$G_{\text{sub}}(T) = \frac{K_a^2}{4\pi m_{\text{sub}} v_{\text{sub}}^3 \rho_{\text{sub}}} C_v^w(T).$$

From this derivation, we conclude that the TBC should have an inverse relationship to the substrate density, speed of sound, and Debye temperature so long as the Debye model captures the phonon dispersion in the substrate.

With these analytical expressions, we map the properties of the materials that constitute the interface to their calculated TBC. We use our $6 \times 5$ dataset (the vDOS of amorphous SiO$_2$ and AlO$_x$ does not follow the $\omega^2$ Debye model, so they are excluded here) to map TBC values to material properties in Figure 3.5a-e. We look at the ratio between Debye temperatures in Figure 3.5a which is often used for bulk 3D-3D interfaces [108, 109], and we see a slight trend when looking at certain 2D layers (graphene and h-BN) but overall the trend across different substrates is weak. In Figure 3.5b-c, we plot the values of TBC against two formulations of the denominator of Eq. 3.6, where we interchange the substrate sound velocity and the substrate Debye temperature as they are related through Eq. 3.8 and $\hbar\omega_D = k_B\Theta_{\text{sub}}$. While we do not see much of a trend in Figure 3.5b, Figure 3.5c starts to show grouping in the top-right corner of the higher TBC interfaces. However, the lower value TBC interfaces are far from the bottom-left corner.

We then recognize that the substrate atomic mass is related to the substrate mass density in Figure 3.5d where we see the TBC values for diamond interfaces shift to the left. While we see a shift in the low TBC value interfaces, there is little change for the interfaces involving GaN, AlN, and SiC. In the next panel (Figure 3.5e) we go a step beyond the
analytical expressions and insert the phonon bandwidth of the flexural branch ($BW_{ZA}$) of the 2D-layer into the denominator. The $BW_{ZA}$ is the frequency range of flexural modes, so that a smaller bandwidth implies a flatter dispersion and denser modes at low frequencies where more heat transfer can occur. As a result, we see a tighter grouping of both the low and high TBC values into the bottom-left and top-right corners, respectively. While we see good correlation in Figure 3.5e, the TBC values for Al$_2$O$_3$ interfaces are outliers. To further regress our TBC values, we split the cube of the substrate sound velocity into one part substrate sound velocity and two parts substrate Debye temperature. It is here where we find the most correlation between the material properties considered and the calculated TBC values with the fewest outliers. We find that the inverse of the product of 2D atomic mass, substrate sound velocity, substrate Debye temperature squared, substrate
mass density, and 2D flexural phonon bandwidth – that is, \(1/(m_{2D}v_{sub}\Theta_{2D}^2\rho_{sub}BW_{ZA})\) – is strongly correlated to the TBC of 2D-3D interfaces with crystalline substrates. Therefore, substrates that are softer and have low sound velocity, low Debye temperature, and low mass density are best for TBC. On the other hand, a 2D layer with lighter atomic mass and a small phonon bandwidth also results in higher TBC.
CHAPTER 4

THERMAL BOUNDARY CONDUCTANCE OF BEYOND-GRAPHENE TWO-DIMENSIONAL MATERIALS ON SiO₂ AND GaN

In this chapter, the temperature-dependent TBC of an additional 8 interfaces is computed with and without the presence of an aluminum oxide encapsulating layer. The 2D materials are silicene, boron arsenide (BAs), blue phosphorus, and black phosphorus. For 3D substrates, we use prototypical amorphous and crystalline materials, SiO₂ and GaN. The TBC values calculated here include internal resistance which is most pronounced in bare-2D/3D interfaces where it is mostly comprised of temperature-dependent anharmonic scattering $\Gamma_{anh}$. The temperature dependence of internal scattering imposes a stronger temperature dependence on the TBC, which is partially lifted when the 2D/3D interfaces are encapsulated. The results show that scattering with the encapsulating layer via $\Gamma_{enc}$ can be much stronger than anharmonic scattering $\Gamma_{anh}$ leading to an increase in TBC and a reduction in its temperature dependence (recall $\Gamma_{int}(\omega, T) = \Gamma_{enc}(\omega) + \Gamma_{anh}(\omega, T)$). The effects of encapsulation are reduced for crystalline substrates where the external TBC is lower, and hence improvements on the internal TBC are less significant.

4.1 Temperature-dependent TBC of uncoated and coated interfaces

The calculated temperature-dependent TBCs of single-layer 2D-SiO₂ and 2D-GaN interfaces with and without AlOₓ encapsulation are shown in Fig. 4.2a-d. We start with a $K_a=2.7 \text{ N.m}^{-1}$ for a Gr/SiO₂ interface that well-reproduces the measured room-temperature value of 42 W.m⁻².K⁻¹ from Yang et al. [5]. To then better compare across materials, we scale $K_a$ such that the vdW coupling per unit cell $g = K_a/S_{2D}$ is the same for all materials.
Figure 4.1: The phonon dispersion of 2D (a) silicene, (b) blue phosphorene, (c) black phosphorene, and (d) boron arsenide. The acoustic and optical branches are shown as red/blue and black lines, respectively. This figure is taken from Ref. [3].

The values of $K_a$ used to produce Fig. 4.2 are summarized in Table 4.1. The trends across various 2D-3D interfaces are driven by a combination of $\Gamma_{sub}$ (i.e., interface quality, $K_a$) and anharmonicity of ZA phonons via $\Gamma_{anh}$. The strong temperature dependence in Fig. 4.2a is governed by the roughly linear temperature dependence of $\Gamma_{anh}$ which dominates $\Gamma_{eff}$ when $\Gamma_{anh} \ll \Gamma_{sub}$. We show the energy-dependent scattering rates for black phosphorene on SiO$_2$ with (solid) and without (dashed) AlO$_x$ encapsulation in Fig. 4.3a. The anharmonic rate for interfaces without encapsulation (black dashed) is relatively weak compared the substrate scattering rate (solid blue) and therefore bottlenecks the overall TBC. As a result, we obtain a temperature dependence in the TBC that follows closely that of the anharmonic scattering of ZA phonons in the 2D material. This temperature dependence of TBC contrasts with the rather weak temperature dependence seen from MD simulations of
silicene and BP interfaces on SiO$_2$ [110, 111]. The predicted values for silicene/SiO$_2$ interfaces agree with Ref. [110] which reports TBC in the range of 23-30 W.m$^{-2}$.K$^{-1}$, but they are several factors (2-3 times) lower than the MD predicted values for BP/SiO$_2$ interfaces in the same study.

When the 2D-3D stacks are encapsulated (Fig. 4.2b), which is often required for many 2D materials to prevent degradation due to harmful atmospheric effects such as oxidation [90, 91], scattering with the encapsulating layer $\Gamma_{enc}$ combines with the anharmonic rate $\Gamma_{anh}$, increasing internal scattering $\Gamma_{int}$, as seen by the solid black and pink curves in Fig. 4.3a. Moreover, similar to $\Gamma_{sub}$ in Eq. (2.15), scattering with the encapsulating layer is temperature-independent and, in general, stronger than internal scattering of ZA phonons. As a result, $\Gamma_{int}$ increases significantly and the resulting temperature dependence follows
the 2D heat capacity of the ZA branch (see Eq. 2.11) which is nearly constant above the Debye temperature $\theta_D = \max(\hbar \omega_{ZA})/k_B$ of ZA phonons (250K or lower in the 2D materials studied here). The TBC of AlO$_x$/2D/SiO$_2$ interfaces shows a noticeable increase when swapping from graphene or hBN to silicene, BAs, BluP, or BP.

Exchanging amorphous SiO$_2$ for crystalline GaN (Fig. 4.2c,d), which has been theoretically proposed as a viable substrate for epitaxial growth of phosphorene allotropes [112], we see a different trend across the 2D materials and we do not see as much improvement upon encapsulation. The reason is that the vDOS of crystalline substrates follows a Debye-model $\omega^2$ dependence [4], as seen in its vDOS in Fig. 4.3b, which leads to poor overlap between the low-lying ZA vDOS of 2D materials. As a result, ZA phonons are not scattered enough by interactions with substrate modes (i.e., $\Gamma_{sub} \ll \Gamma_{int}$) and therefore any increase in the internal scattering rate $\Gamma_{int}$ returns only a negligible increase in the TBC. This is most pronounced in BAs/GaN interfaces where the vDOS overlap is negligible (as seen in Fig. 4.3b).
Table 4.1: The unit cell mass $m_{2D}$ (a.u.), vdW spring coupling constant $K_a$ (N.m$^{-1}$), 2D unit cell surface area $S_{2D}$ (Å$^{-2}$), ZA phonon bandwidth $BW_{ZA}$ (meV), and resonant frequency $\omega_0$ (meV).

<table>
<thead>
<tr>
<th>2D mat.</th>
<th>$m_{2D}$</th>
<th>$K_a$</th>
<th>$S_{2D}$</th>
<th>$BW_{ZA}$</th>
<th>$\omega_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphene</td>
<td>24.02</td>
<td>2.70</td>
<td>5.224</td>
<td>61.48</td>
<td>7.65</td>
</tr>
<tr>
<td>BN</td>
<td>24.00</td>
<td>2.81</td>
<td>5.456</td>
<td>31.05</td>
<td>7.82</td>
</tr>
<tr>
<td>silicene</td>
<td>56.17</td>
<td>7.03</td>
<td>12.65</td>
<td>5.47</td>
<td>8.08</td>
</tr>
<tr>
<td>black phos.</td>
<td>123.9</td>
<td>7.47</td>
<td>14.50</td>
<td>8.33</td>
<td>7.93</td>
</tr>
<tr>
<td>blue phos.</td>
<td>61.94</td>
<td>4.60</td>
<td>8.939</td>
<td>11.28</td>
<td>6.23</td>
</tr>
<tr>
<td>BAs</td>
<td>85.73</td>
<td>5.13</td>
<td>9.961</td>
<td>8.2</td>
<td>5.60</td>
</tr>
</tbody>
</table>

To help further explain the trends seen in Fig. 4.2b relevant quantities are shown in Table 4.1 and attention is given to Fig. 4.3b. The low-energy features of the vDOS of both the 2D material and substrate are of pivotal importance to determining the TBC because $\Gamma_{sub} \propto 1/\omega^2$ and hence low-energy (long-wavelength) ZA phonons are responsible for the majority of interface transport. We show the vDOS of black phosphorene, BAs, SiO$_2$, and GaN in Fig. 4.3b, and we denote the width of the 2D vDOS as $BW_{ZA}$. The 2D vDOS display a forbidden energy region at low energies (approx. $< 5$ meV) which is a consequence of resonant oscillation of the flexural branch caused by the restoring forces of vdW bonding in the long-wavelength regime [113, 114]. The size of this gap varies based on the resonant frequency $\omega_0$ (see Section 2.3.3) [94]. Across the various 2D materials we can see that lower unit cell mass and narrower low-energy ZA vDOS lead to an increase in TBC.

Next, we perform a deeper analysis on the group III-V compounds (e.g., hBN and BAs) where the mass different lattice elements lead to a breaking of degeneracy at the K point between ZA and ZO phonons as seen in graphene [107]. In hBN, where the unit cell mass is not much larger than that of graphene, a large increase in the TBC can be seen under
the assumption that the vdW spring coupling is roughly equivalent between interfaces [4]. This is further pronounced in BAs where the mass difference between the lattice atoms (B and As) is even larger and as a result the vDOS of BAs is pushed even flatter. Despite a moderate increase in the unit cell mass due to the heavier As atom, the TBC increases further for BAs on SiO2 because of the large low-energy vDOS of SiO2 takes advantage of the ultra-soft ZA branch of BAs. Contrast this with BAs on GaN where the TBC is far lesser than the BluP/GaN and silicene/GaN interfaces because of better vDOS overlap. Therefore, group III-V 2D materials like BAs that exhibit an ultra-low lying ZA branch on various crystalline materials may be a promising avenue toward designing interfaces for thermal isolation which may be useful in thermal routing and energy scavenging applications [115]. This data corroborates our previous report [4] (i.e., Chapter 3), where we demonstrated a strong relation between TBC and $1/[m_{2D}v_{sub}\Theta_{sub}^2\rho_{sub}BWZA]$ where $v_{sub}$, $\Theta_{sub}$, and $\rho_{sub}$ are the sound velocity, Debye temperature, and mass density of the substrate. However, one caveat to Fig. 4.2 is in the assumption that each 2D material has nearly equivalent spring coupling per unit cell area. Substrate coupling may vary substantially in practice due to sample quality, growth technique, and processing steps, such as annealing [9].

4.2 Thermal boundary conductance as a function of $K_a$

To disambiguate the role of spring coupling, we compute the TBC as a function of $K_a$ for 2D-SiO2 interfaces with (solid lines) and without (dashed lines) AlOx encapsulation in Fig. 4.4. The symbols represent measured TBC values from Refs. [5, 6, 8, 9, 7] as indicated in Fig. 4.4, which are computed within the 2D/3D vdW TBC model to extract a value of $K_a$. The blue and black vertical lines at $K_a=4.2$ and 8 N.m$^{-1}$ represent DFT-calculated [10] vdW coupling constants for MoS2/OH:SiO2 and Gr/H:SiO2 interfaces, respectively. These values, which are computed for crystalline quartz SiO2, represent upper bounds on the vdW spring coupling between 2D/amorphous SiO2 interfaces involving graphene and MoS2. Hence, this model predicts that the TBC of idealized, well-contacted 2D-3D interfaces...
between Gr (MoS$_2$) and SiO$_2$ could reach values much larger than what has been measured thus far.

For encapsulated 2D-3D stacks we see surprisingly good TBC for silicene, blue phosphorene, hBN, and BAs in the range of $K_a=1$-2 N.m$^{-1}$, which is quite weak (2-3x smaller) compared to the aforementioned first-principles values of vdW coupling of interfaces involving graphene and MoS$_2$. We note here that we observe better TBC for BAs, silicene, and blue phosphorene as compared to graphene and various TMDs at values of $K_a$ extracted from corresponding experiments $[6, 9, 54, 116]$. Specifically, in the region of $K_a=2$-4 N.m$^{-1}$, we see the TBC well-exceeding $\sim 50$ W.m$^{-2}$K$^{-1}$ in most cases. These relatively large TBC values for 2D-3D systems at modest spring coupling constants is a
promising finding for designing thermally robust 2D devices based on beyond-graphene materials. We note that there are no experimental studies measuring the TBC of the 2D materials studied here (not including hBN and graphene). Although, ultrafast pump-probe spectroscopy was used to measure the TBC of bulk-BP/Al interfaces [117] where the TBC was reported to be 60, 150, and 200 W.m$^{-2}$.K$^{-1}$ in the cross-plane, armchair, and zigzag directions, respectively. While on a different 3D substrate, we note that the reported value of 100 W.m$^{-2}$.K$^{-1}$ for AlO$_x$/BP/SiO$_2$ is on par with the values measured in that study. This is a fair comparison since the additional BP layers in the bulk have similar effects as an encapsulating layer on the overall TBC [118].
CHAPTER 5
PREDICTION OF THERMAL BOUNDARY CONDUCTANCE OF 2D-SUBSTRATE INTERFACES USING MACHINE LEARNING

In this chapter, machine learning (ML) is used to develop a streamlined predictive model for 2D/3D vdW thermal boundary conductance. This includes an expansion in our dataset of material dispersions for 2D materials and substrates. Namely, we have added phonon dispersions (or vibrational density of states if the former is unattainable) for MoTe$_2$, WTe$_2$, CaF$_2$, HfO$_2$, Si, Ge, Ti, and polymer polymethyl methacrylate (PMMA). Combined with the materials in the previous chapters, this gives 156 interface pairings (summarized in Fig. 5.2a) for which we compute the TBC over a range of interface vdW coupling constants $K_a = [0.4, 8]$ N.m$^{-1}$ resulting in a dataset of 5460 TBC values. This expanded dataset enables the training of ML algorithms where suitable algorithms for achieving highly accurate ML predictions are identified and sensitivity analysis on material descriptors is performed. We demonstrate that when using an exhaustive list of material descriptors, excellent model fitness showing $R^2 > 0.9$ and root-mean-square error (RMSE) $\epsilon < 15$ MW.m$^{-2}$.K$^{-1}$ can be achieved for: decision-tree, neural network, and Gaussian process regression algorithms. Decision-tree regression is then used to perform sensitivity analysis and select-down a list of material descriptors that are the most influential towards predicting the TBC. Sensitivity analysis determines that the vdW spring coupling constant, 2D thermal conductivity, ZA phonon bandwidth, ZA phonon resonance gap, and the frequency of the first van Hove singularity (for crystal substrates) or Boson peak (for amorphous substrates) are the most influential material descriptors.
5.1 Background

The application of machine learning (ML) in material science over the last two decades has been widely successful leading to new insights and advancements in materials physics, discovery, and device design [119, 120, 121, 122, 123, 124, 125, 126, 127]. More recently, machine learning has been used to investigate the thermal properties of materials [128, 129], including the thermal boundary conductance between 3D/3D [130, 131] and 2D/2D systems [132]. There have been several successful efforts to experimentally measure 2D/3D thermal boundary conductance (TBC) [6, 5, 8, 9, 52, 88] as well as to provide explanations of the underlying physical dynamics through theoretical modeling based on Green’s functions [133, 134, 10, 93], Molecular Dynamics (MD) [83, 22], and the Boltzmann transport equation [86, 4, 135, 136]. However, the vast majority of these studies focus on a few interface pairs involving graphene (Gr), hBN, and transition metal dichalcogenides (TMDs) on SiO₂, while measurements of interfaces involving other substrates (AlOₓ, AlN, and diamond) [52] were primarily done with Gr as the 2D layer. Although these studies represent some of the first investigations and theoretical frameworks of 2D/3D TBC, the literature lacks the breadth of 2D/3D TBC data (both experimental and theoretical) that is required to train most ML algorithms. To date, there are fewer than 50 experimentally measured or theoretically calculated values for different interface pairs [137, 52, 4], which is insufficient to train a predictive model. There is a need to expand the available data so that accurate TBC prediction and methodical materials selection can be accomplished.

5.2 Material descriptors and model training

The general workflow from DFT+pBTE simulations to machine learning model training is depicted in the schematic shown in Fig. 5.1. After we perform exhaustive DFT+pBTE calculations on the 156 interface pairs, we collect material descriptor data to be used in training ML models. The selection of descriptors is initially motivated by our previous study [4] (Chapter 3) where we derived an analytical expression for the TBC by assuming
Figure 5.1: A schematic describing the process of data generation and processing which combines (left) rigorous atomistic simulations that are based on first-principles, (middle) data collection and material descriptor selection, and (right) machine learning analysis.

A Debye model for the vDOS for crystal structured substrates. The analytical expression highlighted several material properties – 2D unit cell mass ($m_{2D}$), ZA phonon bandwidth ($BW_{ZA}$), substrate sound velocity ($v_{3D}$), substrate Debye temperature ($\theta_{3D}$), and substrate mass density ($m_{sub}$) – that strongly correlated with the resulting TBC of the respective 2D/3D interfaces. Machine learning algorithms provide several advantages compared to the analytical analysis in Chapter 3. In particular, both crystalline and amorphous materials can be considered in the regression at the same time, as opposed to the analytical models which apply to crystalline materials only. Further, ML models lend themselves to sensitivity analysis and therefore make it easier to identify impactful material descriptors.

The complete list of material descriptor symbol, definition, and units are shown in Table 5.1. Our descriptors can be described as property and compound descriptors [131] being comprised of physical features of either one of the materials that form the interface (property descriptor) or a feature of the interface itself (compound descriptor, such as the vdW coupling constant). Notable material descriptors used in our work here are the vdW coupling constant (which may be dependent on fabrication/processing and unique to a spe-
Table 5.1: List of material descriptor symbols, definitions, and units.

<table>
<thead>
<tr>
<th>Variable Symbol</th>
<th>Definition</th>
<th>Units</th>
</tr>
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<tbody>
<tr>
<td>$K_a$</td>
<td>van der Waals spring coupling constant</td>
<td>N.m$^{-1}$</td>
</tr>
<tr>
<td>$S_{2D}$</td>
<td>2D unit cell surface area</td>
<td>Å$^{-2}$</td>
</tr>
<tr>
<td>$h$</td>
<td>2D layer thickness</td>
<td>Å</td>
</tr>
<tr>
<td>$m_{2D}$</td>
<td>2D unit cell mass</td>
<td>a.u.</td>
</tr>
<tr>
<td>$\rho_{2D}$</td>
<td>2D mass density</td>
<td>g.cm$^{-2}$</td>
</tr>
<tr>
<td>$N_{atom}$</td>
<td>number of atoms per 2D unit cell</td>
<td>N/A</td>
</tr>
<tr>
<td>$\kappa_{2D}$</td>
<td>2D thermal conductivity</td>
<td>W.m$^{-1}$.K$^{-1}$</td>
</tr>
<tr>
<td>$\theta_{ZA}$</td>
<td>Debye temperature of ZA phonons</td>
<td>K</td>
</tr>
<tr>
<td>$BW_{ZA}$</td>
<td>2D ZA phonon bandwidth</td>
<td>meV</td>
</tr>
<tr>
<td>$\omega_0$</td>
<td>2D ZA resonant frequency gap</td>
<td>meV</td>
</tr>
<tr>
<td>$m_{3D}$</td>
<td>3D atomic mass</td>
<td>a.u.</td>
</tr>
<tr>
<td>$\rho_{3D}$</td>
<td>3D mass density</td>
<td>g.cm$^{-3}$</td>
</tr>
<tr>
<td>$\theta_{3D}$</td>
<td>3D Debye temperature</td>
<td>K</td>
</tr>
<tr>
<td>$v_{3D}$</td>
<td>3D sound velocity</td>
<td>km.s$^{-1}$</td>
</tr>
<tr>
<td>$\omega_{3D}$</td>
<td>boson peak (amorph), 1st van Hove singularity (crystals)</td>
<td>meV</td>
</tr>
<tr>
<td>$aflag$</td>
<td>flag for crystals (0) or amorphous (1) atomic structures</td>
<td>unitless</td>
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The resonant frequency gap $\omega_0 = \sqrt{K_a/m_{2D}}$, the presence of atomic order or disorder in the substrate (aflag), and the location of the first peak in the vDOS of the substrate ($\omega_{3D}$). For crystalline materials, $\omega_{3D}$ is the location of the first van Hove singularity [138]. In amorphous materials, the randomized atomic positions destroy the picture of crystal momentum and causes the van Hove singularities to shift to lower energies resulting in a rounded peak that is called the boson peak [101]. We make note of these material descriptors because they are not typically seen in the literature when training ML algorithms for thermal properties because they are specific to the interface environment.

There are 156 unique 2D/3D pairings for which we compute the TBC on an array of $K_a$ values resulting in a total observation pool of 5460 TBC values which are then randomized and split 70/30 for training and testing data sets. We take the logarithm of the TBC for each observation to reduce the range of target values during training and testing. In addition to separating 30% of the observations for testing alone, a 5-fold cross-validation is performed on each model before the validation RMSE is computed. We use this data to then train
four models that yield high predictive accuracy which are linear with interactions [139],
decision tree [132], neural network [132], and Gaussian process regression [130, 131]. The
motivation for choosing these algorithms is based on their interpretability (relatively small
linear and decision tree algorithms) or predictive accuracy (neural networks and Gaussian
process regression) [126, 140]. Model fitness for each ML algorithm is decided based on
the maximization (towards 1) of the coefficient of determination $R^2$ and the minimization
of the RMSE.

5.3 TBC predictions and model fitness

The room-temperature TBC of each interface pair calculated with our model at a vdW
coupling of $K_a = 2.88$ N.m$^{-1}$ is shown in Fig. 5.2a. Graphene and hBN stand out as the
best performing 2D materials for interface thermal transport with TBC > 10 MW.m$^{-2}$.K$^{-1}$ for
most pairings except for diamond. However, graphene is a semi-metal and hBN is electrically insulating, and so neither can be used as a channel material in FET devices where

![TBC diagram](image)

Figure 5.2: The room-temperature TBC (a) of each 2D/3D pair at a constant value of
spring coupling constant ($K_a = 2.88$ N.m$^{-1}$) is shown. The fitness of a gaussian process
regression model is assessed in (b) where a testing RMSE of 9 MW.m$^{-2}$.K$^{-1}$ is achieved
against DFT+pBTE simulations of TBC for 156 2D/3D interface pairs.
semiconductors with an appropriate bandgap (0.4-2 eV) are required. Out of the semiconducting 2D materials studied here (BAs, BluP, BP, and TMDs), it is found that BluP, BAs, and BP outperform the heavier transition metal dichalcogenides. As for substrate (3D) materials, we find that PMMA, SiO\textsubscript{2}, HfO\textsubscript{2}, and Ge are the four best performing substrate materials for 2D/3D TBC. However, fcc calcium fluoride (CaF\textsubscript{2}), which has been shown to form well-defined vdW interfaces with 2D materials [141], also shows very high TBC (138 MW.m\textsuperscript{-2}.K\textsuperscript{-1}) with hBN. For ultra-high TBC, our calculations highlight BAs/PMMA (polymethyl methacrylate), hBN/CaF\textsubscript{2}, and BAs/SiO\textsubscript{2} as having the highest TBC amongst interfaces calculated here with values of 178, 138, and 115 MW.m\textsuperscript{-2}.K\textsuperscript{-1}, respectively. Of these, only hBN/CaF\textsubscript{2} involves a crystalline substrate while the others are on amorphous substrates. Conversely, diamond, crystalline Al\textsubscript{2}O\textsubscript{3}, and 6H-SiC show TBC less than 10 MW.m\textsuperscript{-2}.K\textsuperscript{-1} for most interface pairs, owing to the mismatch between soft flexural 2D phonons and stiff crystalline substrates, with WSe\textsubscript{2}/diamond being the lowest at 0.18 MW.m\textsuperscript{-2}.K\textsuperscript{-1}. Overall, we find that 2D/3D TBC can span 3 orders of magnitude.

Machine learning models are first trained using the room-temperature TBC data of the 156 interface pairs at only a single value of vdW spring coupling constant. We found that several ML models (decision tree, neural network, and Gaussian process) could predict the TBC with high predictive accuracy RMSE \(<\sim 13\) MW.m\textsuperscript{-2}.K\textsuperscript{-1}. The model fitness for Gaussian process regression with a rational quadratic kernel function is shown in Fig. 5.2b where excellent predictive accuracy is seen. Although sufficient predictive accuracy can be achieved on a small set of 156 datapoints, the resulting ML model cannot determine the importance of the spring coupling constant \(K_a\) nor make accurate predictions if it were to be varied due to unmitigated sample-to-sample variations in interface preparation [6, 54, 9]. Processing steps, such as annealing, have been shown to impact the morphology of the substrate surface [142], which strongly affects vdW spring coupling through average atomic separation between the 2D layer and the substrate surface.
To overcome these limitations here, we compute the TBC for each unique interface over a range of vdW coupling constants spanning \([0.4, 8] \text{ N.m}^{-1}\) resulting in a total of 5460 observations. By using an adjustable \(K_a\) one can span a range of potentially achievable values of TBC provided the required adhesion/coupling can be experimentally achieved. Further, training the ML models on a range of values of \(K_a\) results in a more versatile model that allows one to subsequently predict a range of possible TBC values for any other arbitrary interface. Using the full list of 16 material descriptors, we trained numerous regression models and found the best performing algorithms to be Gaussian process (GPR with a rational quadratic kernel) and wide-neural network (WNN) regression. However,

![Figure 5.3: Machine learning model fitness for (a) linear (with interactions), (b) binary decision-tree, (c) neural network, and (d) gaussian process regression algorithm is shown. The black solid line represents an exact linear fit to the target data, while the grey and green circles represent the training and testing/validation data, respectively.](image-url)
such ML models are often considered complex \emph{black-box} models that can heavily distort and obscure input-output relations [129, 140].

Therefore, the performance of simpler ML models are considered, such as linear and decision tree regression which are known to provide better interpretability when compared to more sophisticated ML models (NN, GPR). The best performing of these simpler ML algorithms are linear with interactions (LRi) and binary decision-tree (DTR) regression. The fitness results for training these four ML algorithms (a-LRi, b-DTR, c-WNN, and d-GPR) is shown in Fig. 5.3 where grey and green circles represent training and testing predictions, respectively. The RMSE and coefficient of determination $R^2$ remains under $\epsilon < 15 \text{ MW.m}^{-2}\text{K}^{-1}$ and above 0.95, respectively, for all algorithms except for linear with interactions. The RMSE is dominated by interface pairings with larger TBC (greater than 10 MW.m$^{-2}\text{K}^{-1}$) which is exampled by the larger RMSE values reported for the LRi ML model in Fig. 3a where larger deviations in predicted values greater than 10 MW.m$^{-2}\text{K}^{-1}$ compared to other ML algorithms can be seen.

5.4 Sensitivity analysis

Next, sensitivity analysis is performed to determine which material descriptors are the most impactful to model training. A decision tree regression model is chosen for the sensitivity analysis since they are well known for their high interpretability [143]. Our sensitivity analysis is performed by iteratively removing material descriptors and determining model fitness (RMSE and $R^2$) each time. If a descriptor is found to improve model fitness when removed, it is then removed for subsequent training cycles. We then repeat the process having removed that descriptor until the model does not improve upon removing any descriptors. This results in a list of the material descriptors that are the most impactful on model accuracy – these descriptors are the vdW coupling constant ($K_a$), 2D thermal conductivity ($\kappa_{2D}$), ZA phonon bandwidth ($BW_{ZA}$), ZA phonon resonance gap ($\omega_0$), and location of first substrate vDOS peak ($\omega_{3D}$).
Figure 5.4: The Pearson correlation coefficients between impactful 5 descriptors and the TBC is shown in (a). Using the reduced set of 5 descriptors to train a binary decision-tree algorithm, the transferability of the model to pairings not used in the training is assessed. Root-mean-square-error (RMSE) and the coefficient of determination ($R^2$) for a binary decision-tree algorithm tested on materials it has not seen listed along the x-axis is shown in (b).

The Pearson correlation coefficients of the most influential material descriptors identified by sensitivity analysis are shown in 5.4a. Pearson correlation coefficients show the linearity between descriptors and the TBC where values closer to ±1 represent strong positive/negative correlation and values close to zero represent low correlation. It can be seen that the ZA resonant frequency gap $\omega_0$ is the most correlated descriptor to the TBC. This is due to two reasons: (1) $\omega_0$ depends on the vdW spring coupling constant $K_a$, which also shows high correlation, and the 2D unit cell mass, and (2) $\omega_0$ impacts the shape of the 2D vDOS at low-energies [94, 114, 86]. The latter affects the substrate scattering rate which has a $1/\omega^2$ dependence (see Section 2.3.1 of Chapter 2). On the other hand, $\omega_{3D}$ has a strong negative correlation and describes the frequency of the first peak of the substrate vDOS – for crystalline materials this is the first van Hove singularity and for amorphous substrates this is the boson peak [144, 101]. These descriptors highlight the dependence of the TBC on the shape of the vDOS on each side of the interface. A complete set of material descriptors used for training ML models is shown in Table 5.1.
We next determine the transferability of decision tree algorithms. Transferability is the ability of the ML model to transfer its displayed predictive accuracy to data it has not been trained on (i.e., data the model has not seen). To do this, 2D and 3D materials are iteratively removed from the training and validation cycles. Subsequent predictions are then performed for those interfaces involving the excluded material. The model fitness parameters for a decision tree algorithm resulting from the removal of each material studied here is shown in Fig. 5.4b. Accurate predictions are seen (RMSE less than 20-30 MW.m\(^{-2}\).K\(^{-1}\) and an \(R^2 > 0.75\) in most cases) for the TBC of removed materials such as silicene, TMDs, nitrides, oxides, and fcc-structures (e.g., Si and CaF\(_2\)). Some outliers are graphene (Gr), boron arsenide (BAs), boron nitride (hBN), germanium (Ge), and PMMA which represent the lightest 2D (having low \(m_{2D}\)), heavy crystalline substrates, and lightest

Figure 5.5: The fitness of (a) linear, (b) binary decision-tree, (c) neural network, and (d) Gaussian process regression algorithms trained using just the 5 impactful descriptors are shown.
amorphous material in our dataset. This merely illustrates the expected limitation that the ML model cannot predict the TBC for interface pairs that lie outside the extrema of material descriptor values. The model fitness of each four ML models when using just the five impactful material descriptors is shown in Fig. 5.5. A clear degradation in the predictive accuracy of LRi is seen. However, the remaining ML models retain high predictive accuracy, showing only a slight increase in the RMSE. This shows that even complex machine learning algorithms, such as WNN and GPR, can still achieve high predictive accuracy when using only five material descriptors.

We note that some of our descriptors (even after sensitivity analysis) rely on specialized knowledge of a material that may not yet be available in materials databases, especially for amorphous materials. However, for many of them there are related works that employ machine learning to accurately predict such descriptor values (e.g., thermal conductivity, boson peak location [145], etc.) from structural and commonly-databased material features. Therefore, machine learning could play an even further role in guiding the classi-

Figure 5.6: RMSE and $R^2$ computed as a function of the number of observations included in the training of a decision tree regression model.
fication and optimization of 2D/3D TBC. For instance, machine learning combined with DFT calculations of van der Waals forces could substantially advance our understanding of the fundamental limits of adhesion, and subsequently thermal transport, at van der Waals interfaces.

### 5.5 Number of Observations and distribution of TBC data

The number of observations needed to train a machine learning model and obtain good predictive accuracy is an important metric to know when data is limited. It is found that the number of observations needed to train fine/dense decision tree algorithms and achieve an $R^2 > 0.9$ is roughly 1500 observations as seen in Fig. 5.6. In our case it is straightforward to expand our dataset using a range for unknown parameters, such as vdW spring coupling constant $K_a$, and the same could be done with temperature. However, experimental data is lacking for a wide-range of interfaces and the added degrees of freedom brought on by the impact of sample fabrication and processing on interface adhesion further complicates model fitting. Therefore, it is advantageous to estimate how much data (and thereby ef-

![Figure 5.7: The distribution of TBC values within our dataset of 5460 observations.](image)
fort) is required before machine learning algorithms can be expected to return accurate predictions when trained on experimental data. Since the parameter space (descriptors) would need to be expanded to include fabrication and synthesis methods, we can take this estimate to be a lower bound on necessary number of experimental observations needed. The distribution of TBC data is shown in Fig. 5.7 where the number of interfaces with a given TBC value are counted. It can be seen that most interfaces have a low TBC. Roughly 75% of interfaces have a TBC lower than 50 MW.m$^{-2}$.K$^{-1}$. The span of our data demonstrates that higher TBC values (> 100 MW.m$^{-2}$.K$^{-1}$) can be achieved at interfaces that are well-matched, having large low-energy substrate vDOS, and with higher coupling $K_a$. 


CHAPTER 6

THERMAL BOUNDARY CONDUCTANCE OF FEW-LAYER AND HETEROSTRUCTURED VAN DER WAALS 2D MATERIALS ON SILICON DIOXIDE

In this chapter, the thermal boundary conductance at van der Waals interfaces between few-layered and heterostructured 2D materials on SiO$_2$ is investigated. First, the phonon dispersion of the few-layered 2D materials (FL-2D) is computed from the analytical solution of a linear chain model (LCM), see Eq. 2.24, and then used to predict the TBC in various FL structures as a function of temperature and thickness. The results show that additional 2D layers in the 2D/3D stack have a similar effect as adding an encapsulating layer. The added layers provide additional thermal reservoirs and modes of vibration (i.e., a channel of transport) for flexural phonons. Room-temperature thickness-dependent calculations reveal that the TBC increases rapidly from the single-layer case but then saturates around 10-15 layers. The TBC of vdW heterostructures (vdWH) is then explored by first numerically solving the LCM of a system comprised of different masses-springs to obtain the phonon dispersion of flexural phonons in the vdWH stack. The phonon dispersion of a 2L/2L MoS$_2$/WSe$_2$ heterobilayer is computed with a frozen-phonon approach and then compared to the dispersion of the same structure obtained using a LCM. The temperature-dependent thermal boundary conductance is then computed for select combinations of vd-WHs.

6.1 Background

Substrate supported single-layered 2D systems typically suffer from low carrier mobility due to scattering with trapped charged impurities at the substrate surface [146, 147].
Adding 2D layers (thereby increasing the 2D-layer thickness) can help screen carriers in layers further from the substrate from charged impurities increasing overall carrier mobility towards the phonon-limited case [146, 148]. However, when adding 2D layers to the stack, other physical properties of the 2D-layer are also modulated, such as the band gap value [149], the type of band-gap (direct to indirect) [150], in-plane thermal conductivity [151], etc. Beyond adding 2D layers of the same composition, different 2D materials can be stacked together forming vertical heterostructures due to the weak vertical inter-layer vdW-coupling between layers. By changing the material composition of layers in the stack, 2D-layer properties can be further tuned and, in some cases, unique properties can arise that are not present in the single-layer or few-layered homogeneous counterparts. The flexibility of mixing together different 2D materials into a vertical vdWH provides an additional degree of freedom to further design enhanced 2D devices.

There are several factors to consider regarding the distribution of electrons in FL-2D and vdWH structures however. In FL-2D stacks, the distribution of carriers ($n$) varies exponentially peaking near the gate and decreasing moving up the stack (assuming a back-gated device). The varying carrier concentration can be treated according to Thomas-Fermi screening theory [152, 153, 154] where it takes an exponential form. On the other hand in vdWH systems, band alignment can confine electrons to particular layer(s) of the stack [37]. A straight-forward example is a graphene/hBN/SiO$_2$ heterostructure where all the electrons travel in the graphene layer due to the large band gap of hBN and lack thereof for graphene. Alternatively, by mixing different TMD monolayers, whose bands align based on their electron affinities, one can confine electrons to a region of layers depending on the composition of each layer. This may lead to a combination of materials that favors both electron transport (by maximizing mobility and conductivity) and heat removal through the substrate (by maximizing the TBC) having a two-fold impact on few-layer 2D-device performance.
Below, the thickness dependence of the TBC for several FL-2D stacks are calculated. The temperature dependent TBC of select vdWHs are also calculated. As discussed in Section 2.3.3 and 2.3.4, the 2D/3D vdW TBC model is adaptable to few-layer/3D interfaces and calculations for mixed vdW heterostructures can be achieved by swapping out the per-layer phonon dispersion for the corresponding 2D material and numerically solving the LCM. SiO$_2$-supported few-layered and heterostructured stacks are considered and emphasis is given to those comprised of transition metal dichalcogenides. Two structures that have been highlighted as strong candidates for photodetection, WSe$_2$/MoS$_2$/WSe$_2$ and WSe$_2$/Gr/MoTe$_2$ [155], are also investigated.

![Figure 6.1: The phonon dispersion of an 18-layer WSe$_2$ stack where the gapped dispersion of the flexural (ZA) branches is shown in (a) in red. The as-calculated ZA branch is shown in blueish gray and the remaining (non-flexural) phonon branches are the black lines. The vDOS is shown in (b) where the contributions to the vDOS from different branches are color coded as they are in (a). The black curve in (b) represents the total vDOS. A close-up of the 18 flexural modes is shown in (c). This figure is adapted from Ref. [55].](image_url)
6.2 Results and Discussion

6.2.1 Phonon dispersion from Linear Chain Model and VASP

The phonon dispersion of a homogeneous 18-layered WSe$_2$ stack is shown in Fig. 6.1a. This dispersion is calculated using the single-layered WSe$_2$ dispersion combined with the analytical solution (see Eq. 2.24) to the linear chain model (LCM) for an N-layer stack. The red curves represent the different branches of gapped flexural vibrational modes for the stack. The gapped flexural phonons frequencies are calculated according to Eq. 2.24 where $K_z$ is the interlayer vdW coupling constant and $K_{sub}$ is the vdW coupling between the 2D-layer and the substrate. The vDOS of the few-layered structure is shown in 6.1b where the contribute from flexural phonons is highlighted in red. A close-up of the zone-center flexural phonons is shown in 6.1c. The interlayer vdW coupling per unit area ($\bar{K}_z$) between 2D-layers was experimentally measured to be $8.63 \times 10^{19}$ N.m$^{-3}$ for both MoS$_2$ and WSe$_2$ [87]. For simplicity, we assume this value across all combination and adjust $K_z$ according to $\bar{K}_z = K_z/S_{2D}$ (See Table 4.1 for example $S_{2D}$ values), although $\bar{K}_z$ could get as low as $1.2 \times 10^{19}$ N.m$^{-3}$ for materials such as graphene. There is good agreement between this few-layered dispersion of WSe$_2$ and the dispersions presented in Ref. [156] which are calculated from first-principles.

The full phonon dispersion of a bilayered vdW heterostructure (i.e., 2L-2L) comprised of MoS$_2$/WSe$_2$ is computed from VASP. A frozen phonon approach is used with a projected augmented wave type pseudopotential that employs a GGA-PBE functional with vdW-corrections [157, 158]. A $3 \times 3 \times 1$ supercell is used for the force calculations with an energy tolerance (EDIFF) of $10^{-5}$ eV. The resulting phonon dispersion from VASP is shown in Fig. 6.2a. The red highlighted branches are to represent the flexural phonon branches, however due to eigenvalue swapping, some branches may be swapped near the zone-center. For comparison, the dispersion for the same structure calculated using a numerical solution to the linear chain model is also plotted. Flexural phonon vibrations of the vdWs heterostructure are calculated by solving a linear chain model in the vertical direc-
Figure 6.2: The phonon dispersion of a 2L-2L MoS$_2$/WSe$_2$ vdW heterostructure computed from VASP is shown in (a). The red lines are used to highlight zone-center flexural phonons. Flexural phonon modes calculated from a linear chain model are shown in (b) where the remaining 8 phonon branches for MoS$_2$ and WSe$_2$ are also shown in gray and blueish gray.

The in-plane phonon dispersion of the isolated single-layer 2D system is calculated from first-principles and used as input to the linear chain model. The dynamical matrix is reconstructed taking layer-wise values of $K_z$, $S_{2D}$, and $m_{2D}$ (Eq. 2.23 and Fig. 2.4b) on each row, and the eigenvalue problem is solved numerically to obtain the flexural phonon frequencies and displacements. The resulting dispersion is shown in Fig. 6.2b where the red curves are the result of the LCM and the remaining dispersion (TA/LA/optical branches) of MoS$_2$ (in grey) and WSe$_2$ (in blueish grey) are shown for comparison to Fig. 6.2a. The phonon frequencies of MoS$_2$ in Fig. 6.2b are noticeably higher compared to the GGA+vdW calculated frequencies in (a). This is expected due to the tendency of LDA functionals to overestimate covalent bonding leading to higher phonon frequency predictions. The two dispersions are otherwise fairly well-matched, lending to the accuracy of employing a linear chain model to estimate the flexural phonon frequencies of 2D vdWHs.
6.2.2 TBC of homogeneous few-layered stacks

Figure 6.3a shows the ZA branch vDOS of single-layer graphene (blue), MoS$_2$ (purple), and WSe$_2$ (orange) alongside the vDOS of amorphous SiO$_2$ (black) and amorphous AlO$_x$ (green). From graphene to WSe$_2$, a reduction in the ZA phonon bandwidth corresponding to a flattening of the ZA branch is seen. Flatter ZA branches are favorable for TBC due to the $1/\omega^2$ dependence of $\Gamma_{sub}$; however, the benefits from a flatter ZA branch can be counterbalanced by heavier 2D layer atoms that decrease $\Gamma_{sub}$ [4]. The external TBC – that is, $G_{ext}(T) = \lim_{\Gamma_{int} \to \infty} G(T) \propto \Gamma_{sub}$ – depends quadratically on the vdW coupling constant $K_{sub}$ which is proportional to the adhesion energy between the 2D material and substrate [81]. Here a constant vdW spring coupling constant of $K_{sub} = 2.7 \text{ N.m}^{-1}$ for all interfaces is assumed and focus on the properties of the materials that comprise the interface rather than on the interface quality itself, which may be highly sensitive to the methods of
Figure 6.4: Thickness-dependent thermal boundary conductance at the room temperature for uncoated (a, c, e) and AlO$_x$-coated (b, d, f) graphene, MoS$_2$, and WSe$_2$ on SiO$_2$ is shown on the left-hand side axes. The per branch, per stack percent contribution to the TBC is shown by the blue and red circles and correspond to the right-hand side axes. The labels for the circles correspond to the ith-branch in the corresponding FL structure. This figure is adapted from Ref. [118].

fabrication [9]. Figure 6.3b–d shows the temperature-dependent total uncoated TBC (solid red), uncoated external TBC (dashed black), and total AlO$_x$-coated TBC (solid blue) for single-layer graphene, MoS$_2$, and WSe$_2$ on amorphous SiO$_2$. Competition can be seen between the heavier mass of MoS$_2$ and WSe$_2$ and their correspondingly flatter ZA branch vDOS’s, where, in comparison with graphene, both TMDCs have smaller TBCs despite having narrower ZA phonon bandwidths. The uncoated total TBC shows a strong temperature dependence indicating that internal scattering, which is linear with temperature, has a dominant role. Weak internal scattering in the uncoated stacks leads to a 52.9%, 53.6%, and 60.7% reduction in the total TBC (red line) for graphene (b), MoS$_2$ (c), and WSe$_2$ (d), respectively. However, upon encapsulation approximately 26.67%, 25.36%, and 29.89% of these losses are regained in the AlO$_x$-coated graphene (f), MoS$_2$ (g), and WSe$_2$ (h) samples due to an increase in internal scattering.
The TBC (solid black) of uncoated and coated few-layered graphene (a,b), MoS$_2$ (c,d), and WSe$_2$ (e,f) is shown in Fig. 6.4 on SiO$_2$ at room-temperature as a function of thickness (number of 2D layers). The right-side axis shows the percent contribution per layer, per stack starting with 1-layer in the top-left and increasing in thickness moving from left to right. The top-most line of blue circles represents the first layer closest to the substrate in each FL stack. The percent contribution from each layer reduces monotonically as the layer moves farther from the substrate. For most FL stacks with more than 6 layers, the first 3-layers contribute the bulk majority to the TBC as indicated by their percent contributions being larger than 10%. For 40-layer stacks, the first three layers for graphene, MoS$_2$, and WSe$_2$ interfaces make up 66%, 54% and 52% of the total effective TBC. Figure 5b,d,f illustrate the effect of the AlO$_x$-coating layer for FL stacks with less than 10 layers where there is a modest increase in the TBC of 58.8%, 55.39%, and 77.6% for graphene, MoS$_2$, and WSe$_2$, respectively. For FL stacks with more than 10 layers, the total TBC begins to plateau as the added TBC contributions from additional layers begin to diminish. Further, the AlO$_x$-coating layer has a negligible effect on the total TBC for stacks with more than 20 layers as the coating layer is sufficiently isolated from the layer closest to the substrate by the additional 2D layers in the FL stack.

6.2.3 TBC of vdW heterostructures

Beyond the calculations performed below, there have been several experimental and theoretical studies that have quantified the TBC of substrate-supported few-layered 2D/3D interfaces [56, 93, 88, 55]. The number of studies on the TBC of substrate-supported 2D vdWHs are fewer but rising in number [115, 159]. A review on thermal transport in 2D vdWHs can be found in Ref. [160]. Suspended 2D vertical heterostructures (2D/2D) should be carefully distinguished from substrate supported (2D/2D/substrate). Raman measurements have been adapted to produce accurate measurements of the TBC at 2D/3D interfaces. A well-known non-equilibrium problem between optical and acoustic phonons in
Figure 6.5: The thickness dependence of room-temperature TBC of MX$_2$ (M=Mo,W and X=S,Se,Te) TMDs on SiO$_2$ is shown in (a). Temperature dependent TBC is shown for WSe$_2$/MoS$_2$/WSe$_2$/SiO$_2$ and WSe$_2$/Gr/MoTe$_2$/SiO$_2$ structures in (b).

the 2D layer was circumvented in [55] by probing the low-frequency shear mode rather than the commonly used high-frequency optical modes. The low-frequency shear modes manifest in the few-layered structure as a result of the additional vibrational modes brought on by the added layers [87]. Further, the unique Raman signature of different 2D layers in a vdWH stack were utilized to determine the per layer TBC in SiO$_2$-supported Gr/TMD vdWH stacks [115].

While there have been some measurements made on the TBC of FL-2D/3D stacks [88, 55], it is less common to find TBC as a function of thickness for these systems due to the challenge of synthesizing many samples with varying thicknesses in one large experiment. Yuan et al. [56] used Raman spectroscopy to measure the thickness dependence of MoS$_2$ on crystal silicon. They show a very weak scaling in the thickness dependence, only reaching past 10 MW.m$^{-2}$.K$^{-1}$ after about 25 layers. This is most likely due to the fact that the substrate is crystalline, which we have shown in Chapters 3 and 4 to have lower TBC, and starts out having a poor TBC for the single-layer 2D/3D case. Ong developed a
theoretical model based on Green’s function to calculate the thickness dependent TBC of 2D/3D systems [93]. There the thermal boundary resistance \( R_k = (TBC)^{-1} \) decreased rapidly from 1L and plateaus at a minimum around 6-8 layers. The thickness-dependence of room-temperature TBC for six TMDs on SiO\(_2\) is calculated within the methods for FL-2D/3D vdW TBC presented in Sec. 2.3.4 and shown in Fig. 6.5a. MoTe\(_2\), WTe\(_2\), and MoSe\(_2\) show the strongest scaling compared to the sulfides and WSe\(_2\).

The temperature-dependent TBC of two vdWH stacks that have shown promise as photodetectors are then calculated, the interfaces of interest are WSe\(_2\)/MoS\(_2\)/WSe\(_2\) and WSe\(_2\)/Gr/MoTe\(_2\) [155]. The TBC results are shown in Fig. 6.5b. The room-temperature TBC is approximately 40 MW.m\(^{-2}\).K\(^{-1}\) and 30 MW.m\(^{-2}\).K\(^{-1}\) for WSe\(_2\)/MoS\(_2\)/WSe\(_2\) and WSe\(_2\)/Gr/MoTe\(_2\), respectively. Previously, hBN has been demonstrated to improve the thermal management of 2D-based devices [159, 161]. Therefore, hBN is added at the bottom of either stack to assess its influence as a thermal management material. The results show a TBC of 150 MW.m\(^{-2}\).K\(^{-1}\) for both WSe\(_2\)/MoS\(_2\)/WSe\(_2\)/hBN and WSe\(_2\)/Gr/MoTe\(_2\)/hBN.

Fig. 6.6a shows a drawing of the 2L heterobilayer, where the numbers next to each layer in (a) represent the per layer TBC in MW.m\(^{-2}\).K\(^{-1}\) where the MoS\(_2\) layers have a significantly higher layer TBC. The band alignment between MoS\(_2\) and WSe\(_2\) is shown in

Figure 6.6: A schematic showing the band alignment between MoS\(_2\) and WSe\(_2\) is shown in (a). The TBC of 2L-MoS\(_2\)/2L-WSe\(_2\) (black) and 2L-MoS\(_2\)/2L-WSe\(_2\) system on SiO\(_2\) is shown in (b). Note the log-scale on the y-axis of (b).
Fig. 6.6b where the larger electron affinity of MoS$_2$ ($\chi_{MoS_2}$) places its conduction band lower than WSe$_2$. This would cause carriers to mostly be in the MoS$_2$ layers, and thus most of the heat dissipated by electrons would originate in the MoS$_2$ layers. The temperature-dependent TBC for the 2L-WSe$_2$/2L-MoS$_2$/SiO$_2$ stack is shown in Fig. 6.6b where the room-temperature TBC can be seen to be roughly 50 MW.m$^{-2}$K$^{-1}$. The TBC of the same structure but with an hBN bottom-layer is also shown for comparison where the TBC reaches as high as 148 MW.m$^{-2}$K$^{-1}$ at room-temperature.
CHAPTER 7
CONCLUSION

In this dissertation, a theoretical framework for computing the 2D/3D vdW thermal boundary conductance (TBC) from first-principles phonon dispersion data was presented and employed to study a wide range of 2D/3D interface pairs. The different phase spaces (2D or 3D) on either side of the interface leads to only trivial solutions to interface phonon transport within canonical phonon interface models. Therefore in Chapter 2 the differences between canonical phonon interface transport models (AMM/DMM) for same-dimensional (3D/3D) interfaces and a new theoretical model for 2D/3D vdW interfaces were highlighted. The key takeaway is that phonon transport across 2D/3D interfaces is facilitated by flexural phonons that propagate in-plane but displace atoms vertically (or perpendicular to the substrate normal).

In Chapter 3, the importance of overlap between the 2D/3D vibrational density of states was highlighted and shown to vary the external TBC by several orders of magnitude. In general, amorphous materials which display a low-energy peak in their vibrational density of states, called the boson peak, have higher TBC than interfaces with crystalline substrate. The peak represents the vibrational modes that typically comprise the first van Hove singularity of the crystalline counterpart. However, due to the randomization of atomic positions, the phonon modes that make up the van Hove singularity are redistributed to lower frequency modes in the amorphous material. The composition of the substrate can impact where the boson peak occurs, and a lower boson peak location can greatly improve the TBC for most interface pairings. For example, the boson peak occurs at 10 meV for SiO$_2$.
as compared to 20 meV for AlO$_x$, and as a result the TBC of 2D/SiO$_2$ interfaces are either equivalent to or better (by a factor of 1.33 or 2 in certain cases) than 2D/AlO$_x$ interfaces.

Anharmonic scattering of flexural phonons and its impact on the 2D/3D TBC were explored in Chapter 4. Since interface transport is facilitated by flexural phonons, the rate at which other phonons scatter into flexural phonon modes presents an additional resistance towards interface transport. It was shown that encapsulation increases TBC and reduces temperature dependence by aiding in ZA phonon replenishment. Comparisons are made between different 2D materials by assuming the same substrate coupling constant per unit area for each interface pair. The results showed that blue phosphorus and hBN perform well (with RT TBC of 55 and 60 MW.m$^{-2}$.K$^{-1}$) with no encapsulation, while BAs and silicene performed best on SiO$_2$ when AlO$_x$ encapsulation was present with RT TBC values above 150 MW.m$^{-2}$.K$^{-1}$ at couplings $K_a = 5.13$ and = 7 N.m$^{-1}$. The results showed overall that several beyond-graphene materials, such as silicene and BAs, may have a TBC higher than that of graphene and hBN.

In Chapter 5, the dataset of 2D/3D pairings generated throughout this dissertation expands again culminating to a total of 156 interface combinations. Machine learning algorithms are then applied to the 2D/3D vdW TBC problem. Good predictive accuracy (RMSE $\leq 13$ MW.m$^{-2}$.K$^{-1}$ and $R^2 > 0.95$) amongst decision tree, Gaussian process, and neural network regression is demonstrated when using a list of 16 material descriptors. Sensitivity analysis determines that the TBC is most sensitive to vdW spring coupling constant, 2D thermal conductivity, flexural phonon bandwidth, vdW resonant gap $\omega_0$, and the frequency of the first peak in the substrate vDOS. Decision tree, Gaussian process, and neural network regression algorithms show good predictive accuracy (RMSE $< 15$ and $R^2 > 0.95$) with only these 5 material descriptors. At room-temperature and a vdW substrate coupling constant of $K_a = 2.8$ N.m$^{-1}$, the best performing 2D materials (aside from graphene and hBN) are blue phosphorus, silicene, and BAs. On the other hand, the worst performing 2D materials were TMD tellurides (MoTe$_2$ and WTe$_2$). Notably, we see good TBC for in-
terfaces with crystal Ge and CaF$_2$ which perform similarly to amorphous HfO$_2$ and better than amorphous AlO$_x$.

In Chapter 6, calculations of TBC between few-layered and heterostructured 2D/3D interfaces were presented. The room-temperature TBC of few-layered 2D/3D systems increases with increasing thickness, but the knee in the TBC vs. thickness curve occurs at different thicknesses depending on the 2D material. Encapsulation with a passivation layer improves room-temperature TBC for single and few-layered stacks up to $\sim$15 layers where it becomes negligible. It was shown that bare TMD tellurides and MoSe$_2$ have the best TBC scaling with 2D-layer thickness reaching values around 50-60 MW.m$^{-2}$.K$^{-1}$ around 8-12 layers. A linear chain model (LCM) was shown to well-reproduce the flexural phonon frequencies of a vdW heterostructure by making comparisons with the heterostructure dispersion calculated from VASP using a supercell approach. A LCM model was then used to calculate the flexural phonon dispersion of 2D vdW heterostructures for subsequent TBC calculations. The TBC of select 2D vdW heterostructures was calculated where stacks of WSe$_2$/MoS$_2$/WSe$_2$, WSe$_2$/Gr/MoTe$_2$, and 2L-WSe$_2$/2L-MoS$_2$ on SiO$_2$ showed values of 40, 35, and 52 MW.m$^{-2}$.K$^{-1}$, respectively. It was then shown that adding hBN as a bottom-layer to these stacks greatly improves the TBC as high as 140-150 MW.m$^{-2}$.K$^{-1}$.

This work provides a theoretical framework for assessing the thermal boundary conductance of many 2D/3D interfaces. Several calculations corroborate well with experimentally measured values [9, 55, 88]. However, more work is needed to address the issue of interface adhesion/coupling between different interfaces. Indeed, little is known about the adhesion energy between different single 2D layers and 3D substrates and how it could be improved systematically. Furthermore, numerical models capable of computing van der Waals coupling (a component of adhesion energy) are still limited to small supercell sizes and idealized atomic positions. It should be added that there exists no measured values of TBC for many of the interfaces covered throughout this dissertation. Therefore there is more work to be done in both measuring different interfaces, and in advancing measure-
ment techniques to better capture the physics of interface thermal transport in 2D/3D vdW systems.
BIBLIOGRAPHY


