Thermal conductance of graphene/hexagonal boron nitride heterostructures

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The lattice-based scattering boundary method is applied to compute the phonon mode-resolved transmission coefficients and thermal conductances of in-plane heterostructures built from graphene and hexagonal boron nitride (hBN). The thermal conductance of all structures is dominated by acoustic phonon modes near the Brillouin zone center that have high group velocity, population, and transmission coefficient. Out-of-plane modes make their most significant contributions at low frequencies, whereas in-plane modes contribute across the frequency spectrum. Finite-length superlattice junctions between graphene and hBN leads have a lower thermal conductance than comparable junctions between two graphene leads due to lack of transmission in the hBN phonon bandgap. The thermal conductances of bilayer systems differ by less than 10% from their single-layer counterparts on a per area basis, in contrast to the strong thermal conductivity reduction when moving from single- to multi-layer graphene. Published by AIP Publishing.

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I. INTRODUCTION

Since its discovery, graphene has been the subject of intense experimental and theoretical study.\(^1\) The lack of an electronic bandgap, however, has stymied graphene’s application in nanoelectronic devices. An avenue to graphene-based materials with a tunable bandgap is in-plane (IP) heterostructures built with other two-dimensional materials, such as hexagonal boron nitride (hBN). Using chemical vapor deposition, researchers have fabricated graphene/hBN heterostructures such as superlattices to a high degree of precision.\(^2,3\)

Due to the need to dissipate heat in nanoelectronic devices, understanding the thermal properties of graphene/hBN heterostructures is critical. Thermal transport in graphene and hBN is dominated by phonons,\(^4\) and significant experimental and theoretical work has been done on bulk and nanostructured samples.\(^4–15\) Suspended graphene has an exceptionally high thermal conductivity, experimentally measured to be in the range of 2600–5300 W/m K at room temperature.\(^4,7,8\) Theoretically and computationally, room temperature values as high as 10 000 W/m K have been reported.\(^5,6\) Using an exact solution to the Boltzmann transport equation and input from first principles calculations, Fugallo et al. suggested a maximum value of 3600 W/m K for naturally occurring graphene and 4300 W/m K for isotopically pure graphene.\(^9\) Graphene supported by a substrate has a lower thermal conductivity. A computational study reported a value of 2450 W/m K,\(^11\) while experimental values are reported to be between 370 and 600 W/m K.\(^12,13\) Wang et al. measured the thermal conductivity of bilayer hBN to be 600 W/m K,\(^14\) while computational studies report the intrinsic single-layer hBN thermal conductivity to be as high as 800 W/m K.\(^15\)

Thermal transport across in-plane interfaces between graphene and hBN has not been extensively studied. To date, no experimental measurements have been made. Computational studies have been performed, all using the Tersoff potential.\(^16–20\) Jiang and Wang\(^16\) used nonequilibrium (NE) molecular dynamics (MD) simulation to study in-plane islands of hBN embedded within a graphene sheet. They observed that the reduction of heat current across these structures varied linearly with the perimeter of the embedded object. Zhu and Ertekin performed NEMD simulations of armchair-aligned graphene/hBN superlattices. They studied periods ranging from 2 to 500 unit cells (0.5 to 125 nm at a temperature of 300 K). They observed a minimum in thermal conductivity at a period of 10 unit cells, suggesting that interference effects involving superlattice phonons are significant at such small periods. They also independently predicted an isolated armchair graphene/hBN interface conductance of 2.59 GW/m\(^2\) K. da Silva et al.\(^18\) used equilibrium MD simulations and normal mode decomposition to compute phonon lifetimes in armchair- and zig-zag-aligned graphene/hBN superlattices with up to twenty unit cells in the period. Their results indicate that the minimum in thermal conductivity is due to a reduction in the phonon group velocity, a result that has been observed in other superlattice systems.\(^21–23\)

Due to the high Debye temperature of graphene (2300 K for in-plane modes\(^24\)), its room temperature thermal transport properties are strongly dependent upon quantum statistical effects, which cannot be captured by the MD techniques. Jiang and Wang recognized this limitation and explored graphene/hBN interfaces using the atomistic Green’s function (AGF) technique,\(^16\) which is a harmonic, lattice-based, transfer matrix approach that can naturally include quantum statistics. They calculated the thermal conductance of armchair and zig-zag graphene/hBN interfaces to be 3.5 and 6.9 GW/m\(^2\) K at a temperature of 300 K. Ong and Zhang\(^19\) studied the armchair graphene/hBN interface using the AGF technique and found a thermal conductance of 3.59 GW/m\(^2\) K at a temperature of 300 K, in good agreement...
with Jiang and Wang. Building off of theoretical contributions made by Huang et al., Ong and Zhang computed transmission coefficients for phonon modes in the non-primeval rectangular Brillouin zones of graphene and hBN. They quantified the effect of off-normal phonon incidence on the transmission coefficient and decomposed the thermal conductance into contributions from transverse, longitudinal, and flexural modes. More recently, using the same method, Ong et al. calculated the thermal conductance of the boron (nitrogen) bonded zig-zag interface configuration to be 3.05 (3.42) GW/m²K at a temperature of 300 K.

The objective of this work is to investigate phonon transport across a variety of technologically relevant hetero-structures built from graphene and hBN by calculating the modal contributions to the thermal conductance using quantum statistics and the scattering boundary method (SBM). In Sec. II, we review the Landauer model of the interface, the geometry and configuration of the junctions considered, and the empirical potentials used to model the atomic interactions. In Sec. III, we present and discuss results for (i) ideal interfaces between graphene and hBN along armchair and zig-zag directions, (ii) finite-length graphene/hBN superlattices, and (iii) substrated and bilayer junctions. Thermal transport in the latter two configurations has not previously been investigated. We summarize our findings in Sec. IV.

II. THERMAL CONDUCTANCE MODEL

A. Landauer formalism

We model a junction as a scattering source positioned between two phonon emitters, leading to a three-part domain composed of the left lead, the junction, and the right lead. The left and right leads are semi-infinite, behave as bulk crystals, and are at thermal equilibrium at temperatures $T_L$ and $T_R$. Any deviations from equilibrium are so small that they can be ignored. Without loss of generality, we impose that $T_L > T_R$ so that the net heat flow is from the left lead to the right lead through the junction. If we assume that the temperature difference $T_L - T_R$ is small so that $T_L \approx T_R = T$, the thermal conductance due to ballistic transport of phonons from the left lead to the right lead through the junction, $G$, can be written using the Landauer formula:

$$G = \frac{1}{\Delta} \int_{\mathbf{k} \in \text{first Brillouin zone}} \sum_{\nu} f_{BE}(\mathbf{k}, \nu) \Re \omega(\mathbf{k}, \nu) \frac{\partial \Re \mathbf{F}(\mathbf{k}, \nu)}{\partial T} \mathbf{z}(\mathbf{k}, \nu) \, d\mathbf{k}. \quad (1)$$

The integral is taken over the first Brillouin zone of the left lead and the summation is taken over the phonon modes $\nu$ at a particular wavevector $\mathbf{k}$, which have a positive group velocity component $v_x(\mathbf{k}, \nu)$ in the cross-interface (i.e., $x$) direction. $\omega(\mathbf{k}, \nu)$ and $\mathbf{z}(\mathbf{k}, \nu)$ are the frequency and transmission coefficients associated with the phonon mode at $(\mathbf{k}, \nu)$, and $f_{BE}$ is the Bose-Einstein distribution. $\Delta$ is the out-of-plane (OP) thickness of the junction, which is 3.4 Å for single layer systems and 6.8 Å for bilayer systems.

The terms within Eq. (1) can be split into three parts. First, the integral is performed numerically by discretizing the hexagonal first Brillouin zone into a 40 000-point uniform rectangular grid. Second, $\omega(\mathbf{k}, \nu)$ and $v_x(\mathbf{k}, \nu)$ are bulk crystalline properties that are determined via harmonic lattice dynamics calculations. Third, the $\mathbf{z}(\mathbf{k}, \nu)$ are junction properties that are determined by the SBM,26–30 for which details are provided in Appendix A.

All results presented in this paper are at a temperature of 300 K. We assume that phonon scattering in the junction involves only two-phonon processes that conserve energy and that phonon momentum is conserved up to the periodicity of the junction. Details regarding the application of the conservation rules are provided in Appendix B. The uncertainty in our thermal conductance predictions is quantified by considering the convergence of thermal conductance with the size of the junction.

B. Junction configurations and force constants

The required inputs to the SBM are the atomic structure of the junction and the second-order (i.e., harmonic) force constants that describe the atomic interactions in and between the leads and the junction. A list of all junctions considered is provided in Table I. The structure of the armchair and zig-zag graphene/hBN interfaces is shown in Fig. 1. Experimental interfaces may gradually change lattice constant away from the interface or relieve stress with defects along the interface. These effects are difficult to capture in

<table>
<thead>
<tr>
<th>Type</th>
<th>Left lead</th>
<th>Right lead</th>
<th>Junction</th>
<th>Mixing</th>
<th>Layering</th>
<th>Junction conductance (GW/m²K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IA</td>
<td>G</td>
<td>G'</td>
<td>Armchair</td>
<td>None</td>
<td>Single</td>
<td>5.56 ± 0.22</td>
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<tr>
<td>IZ</td>
<td>G</td>
<td>G'</td>
<td>Zig-zag</td>
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<td>Single</td>
<td>5.46 ± 0.22</td>
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<tr>
<td>IIA</td>
<td>G</td>
<td>BN</td>
<td>Armchair</td>
<td>Terroff</td>
<td>Single</td>
<td>3.67 ± 0.15</td>
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<tr>
<td>IIA-S</td>
<td>G</td>
<td>BN</td>
<td>Armchair</td>
<td>Terroff</td>
<td>Substrate, $l_z = 16$ N/m</td>
<td>3.16 ± 0.13</td>
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<td>G</td>
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<td>Zig-zag</td>
<td>Terroff</td>
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<td>3.70 ± 0.15</td>
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<td>G</td>
<td>BN</td>
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<td>Terroff</td>
<td>Substrate, $l_z = 16$ N/m</td>
<td>3.19 ± 0.13</td>
</tr>
<tr>
<td>IIIA</td>
<td>G</td>
<td>BN</td>
<td>Armchair $2 \times 2 \times n$ Superlattice</td>
<td>Terroff</td>
<td>Single</td>
<td>See Fig. 5</td>
</tr>
<tr>
<td>G</td>
<td>G</td>
<td>Armchair $2 \times 2 \times (n + 1/2)$ Superlattice</td>
<td>Terroff</td>
<td>Single</td>
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<td></td>
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<td>BN-BN</td>
<td>Armchair</td>
<td>Terroff+LJ</td>
<td>Bilayer</td>
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<tr>
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<td>G-G</td>
<td>BN-G</td>
<td>Armchair</td>
<td>Terroff+LJ</td>
<td>Bilayer</td>
<td>4.31 ± 0.39</td>
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</tbody>
</table>

TABLE I. Junction configurations. G and BN indicate the Lindsay and Broido35 and Kinaci et al.36 Tersoff interaction parameters for graphene and hBN. G’ indicates a system using graphene Tersoff parameters but with hBN atomic masses. In cases where both graphene and hBN use the same Tersoff parameters, no cross-interface mixing is used. Otherwise, appropriate mixing rules are applied.
atomistic modeling as they increase the system size to a point where calculations become computationally intractable. Following the approach of Ong et al., the lattice mismatch between graphene and hBN is resolved by isotropically straining the graphene, which has an unstrained lattice constant of 1.4388 Å, by 0.2363% to match the hBN lattice constant of 1.4422 Å. The phonon dispersions for graphene and hBN using the two-atom primitive unit cell along high-symmetry directions are plotted in Fig. 2. Of note is the phonon bandgap in hBN between 215 and 235 Trad/s.

Type I junctions contain a perfect armchair (IA) or a nitrogen-bonded zig-zag (IZ) interface between graphene and hBN. The masses of the three atomic species are the correct physical values, but the Tersoff parameters used for all interactions are identical. Specifically, those published by Lindsay and Broido for graphene with parameters fit to the bulk dispersion generated from first principles density functional theory calculations. The phonon dispersions for graphene and hBN using the two-atom primitive unit cell along high-symmetry directions are plotted in Fig. 2. Of note is the phonon bandgap in hBN between 215 and 235 Trad/s.

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Type II junctions are geometrically identical to Type I junctions, but we instead use Tersoff parameters specific to graphene and hBN (also obtained by fitting the bulk dispersion to first principles calculations). At the interface, the cross-species interaction parameters are computed according to the standard Tersoff mixing rules and we use the same parameters for the B-N-B and N-B-N angular bonds. The introduction of mixing makes Type II junctions a more realistic model of graphene/hBN interfaces than Type I junctions. In junctions IIA-S and IIZ-S, an on-site potential is added to model the presence of a substrate. For the ith atom in the Nth unit cell, this potential has the form,

\[ U_{\text{Substrate,N,i}} = \frac{1}{2} k z_{N,i}^2 \]

where \( z_{N,i} \) indicates the displacement along the z (i.e., out-of-plane) direction. \( k \) is chosen to be 16 N/m to represent a typical van der Waals interaction between single-layer graphene and a substrate.

Type III junctions are finite-length superlattices composed of alternating layers of graphene and hBN. The armchair-aligned superlattice unit cell is built from two atomic layers of hBN attached to two layers of graphene, forming a 2 × 2 unit cell. The unit cell is then repeated n times to form a 2 × 2 × n junction, where n ranges from 1 to 18. These 2 × 2 × n junctions have mismatched graphene and hBN leads. To study the effect of having matched leads, each 2 × 2 × n junction has a 2 × 2 × (n + 1/2) counterpart,
which has an additional two atomic layers of hBN, such that both leads are graphene. The interatomic interactions in the Type III junctions are the same as those in the Type II junctions.

Type IV junctions are bilayer systems created using AB (Bernal) stacking.\textsuperscript{39} The phonon dispersions of the corresponding bulk leads are calculated using the primitive four-atom unit cell. Type IV-A-1 is an armchair graphene/hBN interface over an identical armchair graphene/hBN interface. In Type IV-A-2, the bottom layer is graphene and the top layer is an armchair hBN-graphene interface. The intralayer interactions in the Type IV junctions are identical to those used in the Type II and Type III junctions, and the interlayer interactions are modeled using a 12–6 Lennard-Jones potential with $\epsilon$ and $\sigma$ values of $3.85 \times 10^{-22}$ J and 3.4 Å.\textsuperscript{30}

III. RESULTS

A. Junction types I and II: Cross-interface interaction

The acoustic mismatch and diffuse mismatch models for predicting interface thermal conductance\textsuperscript{31} ignore the cross-interface interaction. They instead attempt to describe interfaces using only the bulk properties of the adjoining materials. It is well-known that these techniques can be inaccurate when compared to ones that incorporate a detailed cross-interface interaction.\textsuperscript{30,42–44} We use the SBM to quantify the difference in the thermal conductance between a model where only mass properties differ (Type I) to a higher-fidelity model that incorporates mixed interactions across the interface (Type II).

In Type I junctions, the predicted thermal conductance is $5.56 \pm 0.22$ GW/m$^2$K for armchair and $5.46 \pm 0.22$ GW/m$^2$K for zig-zag. In Type II junctions, the predicted thermal conductance is $3.67 \pm 0.15$ GW/m$^2$K for armchair and $3.70 \pm 0.15$ GW/m$^2$K for the boron-bonded zig-zag. For the zig-zag junction, the difference in the predicted thermal conductances between the nitrogen- and boron-bonded variants is small enough as to be within their uncertainties, as expected based on the choice of Tersoff parameters discussed in Section II.B. All subsequent results are for boron-bonded zigzag interfaces. Even with an identical interface geometry, the addition of a physically realistic cross-species interaction and a more accurate potential for hBN reduces the predicted thermal conductance by $40\%$–$50\%$. If classical statistics are used in the evaluation of Eq. (1), the thermal conductances of Type IIA and Type IIZ junctions are $11.6 \pm 0.46$ and $12.0 \pm 0.48$ GW/m$^2$K, three times the values predicted using quantum statistics. The use of the correct Bose-Einstein statistics is thus critical when predicting thermal conductance at a temperature of 300 K.

The Type IIA armchair junction thermal conductance is within $4\%$ of the value reported by Ong and Zhang (3.52 GW/m$^2$K).\textsuperscript{19} They also used graphene- and hBN-specific Tersoff potentials and mixing rules at the interface, but with a parameter set that distinguishes between N-B-N and B-N-B angular bonds. In a subsequent study using the same potential,\textsuperscript{20} Ong et al. predicted the zigzag junction thermal conductance to be $3.42$ GW/m$^2$K (nitrogen-bonded) and 3.05 GW/m$^2$K (boron-bonded). This difference can be attributed to their choice of potential. These values are $8\%$ and $20\%$ smaller than our prediction for the zig-zag interface, which, as noted above, does not depend on the bonding. Given the agreement between our armchair prediction and that of Ong and Zhang, this discrepancy between the zigzag predictions is most likely a result of the different treatments of the N-B-N and B-N-B angular bonds.

The Landauer integrand [Eq. (1)] throughout the first Brillouin zone is shown for the Type I junctions in Figs. 3(a) and 3(b) and for the Type II junctions in Figs. 3(c) and 3(d). Despite the significant differences in how the integrands are distributed across the first Brillouin zone, the total thermal conductances of the armchair and zig-zag interfaces are within their uncertainties for each type. As expected, common to all integrands is symmetry about $\kappa_x = 0$ and asymmetry about $\kappa_x = 0$. Type I junctions have larger integrands throughout the first Brillouin zone when compared to Type II junctions and a slower decrease in the integrand from the $\Gamma$-point to the zone edge. This effect is due to the homogeneous interaction environment in Type I, which is broken by the Tersoff mixing rules in Type II. Such a homogeneous environment allows the transmission coefficients to be higher for most modes.

All Type II integrands show significant contributions to thermal conductance for $\kappa_y > 0$ (89\% and 92\% of the total for Types IIA and IIZ). The most significant contributions to thermal conductance come from wavevectors near the $\Gamma$-point, where the acoustic modes are highly populated and have high group velocities and transmission coefficients. In fact, 60\% of the thermal conductance for both Type II junctions comes from acoustic phonon modes with frequencies less than 100 $\text{Tad}/\text{s}$. The contribution decays for large ratios of $|\kappa_y/\kappa_x|$ (i.e., large incidence angles) and large wavevector magnitudes.

The small contribution from the left half of the first Brillouin zone ($\kappa_x < 0$) is because the majority of those modes have a negative cross-interface group velocity $v_{g_x}$. These modes do not contribute to the summation in Eq. (1). As shown in Figs. 3(a)–3(d), for modes with $\kappa_x < 0$, the only contributors to thermal conductance are the three optical branches with positive $v_{g_x}$ near the zone edge along K-$\Gamma$ and, to a lesser extent, M-$\Gamma$. In both Type II junctions, the Landauer integrand extinguishes for all wavevectors greater than 1 Å$^{-1}$, with the exception of small contributions at the K points. The zig-zag interface differs from the armchair interface in the drop off of the Landauer integrand with respect to incidence angle. This drop off occurs sharply at $|\kappa_y/\kappa_x| = 1$ for the zig-zag case, while there is little angular drop off in the armchair case.

The accumulation of thermal conductance with respect to mode frequency for the armchair interface is plotted in Fig. 4(a). The zig-zag interface is qualitatively identical. We distinguish between in-plane (IP) and out-of-plane (OP) modes by projecting the real portion of the normalized mode eigenvector onto the $z$ unit vector. If the result is greater than 0.5, we consider the mode OP; otherwise, we consider it IP. The OP modes, which are a third of all modes, contribute 32\% to the total thermal conductance. The modal contributions to thermal conductance are plotted in Fig. 4(b). At frequencies near zero (i.e., the $\Gamma$-point), the OP modes
contribute nothing as the \( z \)-acoustic (ZA) branch has zero group velocity due to its quadratic shape (see Fig. 1(a)). Their contributions peak at 40 Trad/s due to the increasing group velocity but decreasing Bose-Einstein population. The OP thermal conductance accumulation saturates near 150 Trad/s, corresponding to the highest frequency of graphene’s ZA branch. There are steep drop offs in the conductance contribution of the OP modes at 50–100 Trad/s and between 110 and 140 Trad/s. These drop offs are due to the changes in the transmission coefficient, which often vary dramatically between near unity and zero, and stand in contrast to the lack of modal transmission at 215–235 Trad/s, which is due to the hBN bandgap. Although most of the OP contribution to thermal conductance comes at frequencies lower than 75 Trad/s, IP contributions are more evenly distributed throughout the frequency range. At low frequency, individual IP modes contribute highly, but there is a low density of states. Between 100 and 200 Trad/s, the IP density of states increases, but the single mode contributions decrease due to low group velocity. Only IP modes exist above the hBN bandgap and are responsible for all transmission above 235 Trad/s.

B. Junction type III: Finite superlattices

The thermal conductance of the graphene/hBN superlattice junctions as a function of the number of periods is plotted in Fig. 5. The addition of a single \( 2 \times 2 \) superlattice period into a perfect armchair interface between graphene...
and hBN decreases the junction thermal conductance by 10% from 3.67 to 3.24 GW/m²K. This decrease is much smaller than the 66% reduction predicted from a series conductance model that assumes that the introduction of a single superlattice period increases the number of isolated graphene/hBN interfaces from one to three. The thermal conductance continues to decrease as more periods are added. The rate of decrease becomes smaller as the period number increases. For ballistic transport (as assumed here) in the limit of a large number of periods, the thermal conductance will converge to a value representative of an infinite superlattice. We see this convergence as the superlattice approaches 18 periods, with matched and mismatched trends converging to 2.2 and 2.1 GW/m²K. As was the case with the Type I and Type II junctions, acoustic modes near the Γ point dominate in their contribution to the thermal conductance of superlattice junctions (see Figs. 3(a) and 3(f)). At all period numbers considered, modes less than 100 Trad/s in frequency account for no less than 71% of the total thermal conductance.

The matched leads [2 × 2 × (n + 1/2)] superlattice junctions consistently have higher thermal conductance than the corresponding mismatched leads (2 × 2 × n) junctions. Thus, despite having an additional two atomic layers within the junction, changing the leads to graphene/graphene from graphene/hBN causes the thermal conductance to be greater than that of the shorter mismatched case. We previously observed this effect in finite superlattice junctions built from Lennard-Jones solids. Though the current system differs from that study in that it is two-dimensional and incorporates cross-interface interaction mixing, the effect is still observed. The origin of this effect can be understood by considering the distribution of the Landauer integrand across the first Brillouin zone for the 2 × 2 × 14 and 2 × 2 × 14.5 cases. As shown in Figs. 3(e) and 3(f), the superlattice junction integrand distributions contain an abundance of peaks and valleys, in contrast to those for the simple interfaces shown in Figs. 3(a)–3(d), which have a single, central peak at the Γ point and uniform decay. This added structure is caused by interference effects in the superlattice junctions that are absent from the simple interfaces.

The difference between the matched and mismatched lead superlattice junctions is more subtle. The two cases differ primarily due to a band of high transmission found in the matched case forming an arc starting at (κx, κy) = (0.5, –1.5) Å⁻¹, going through (1.4, 0) Å⁻¹, and ending at (0.5, 1.5) Å⁻¹. This band is absent from the mismatched case and corresponds to phonon transmission from the highest transverse acoustic branch and second to highest transverse optical branch in graphene [see Fig. 1(a)]. Between 215 and 235 Trad/s, these two graphene branches have no matching branches in hBN due to its bandgap. As a result, in the mismatched lead cases, there are no energy conserving transmission pathways available to these phonon modes.

C. Junction types II-S and IV: Substrates and bilayers

A simple model for estimating the junction thermal conductance of a bilayer system is to consider the two layers as independent parallel channels. Because we report thermal conductance on a per area basis [see Eq. (1)], the thermal conductance G_{Parallel} is then the arithmetic average of the two isolated single layer conductances, G_{Top} and G_{Bottom}

\[ G_{Parallel} = \frac{G_{Top} + G_{Bottom}}{2}. \]  

(3)

In reality, interactions between the layers cause the actual thermal conductance G to deviate from \( G_{Parallel} \) by

\[ G = G_{Parallel} + \Delta G_{Interaction}. \]  

(4)

where \( \Delta G_{Interaction} \) is negative. We quantify \( \Delta G_{Interaction} \) by comparing the thermal conductances of bilayer Type IV and substrated II-S junctions to those of the Type II junctions coupled through the parallel transport model.

We consider two bilayer systems. The Type IVA-1 junction is a graphene/hBN armchair interface over a identical graphene/hBN armchair interface, while the Type IVA-2 junction is a graphene/hBN armchair interface over a layer of graphene. In both cases, zone-center acoustic phonon modes are again the dominant contributors to the thermal conductance. Modes with frequencies less than 100 Trad/s in Type IVA-1 and Type IVA-2 junctions contribute 72% and 78% to the total. For the Type IVA-1 junction, G_{Top} is identical to G_{Bottom} and is 3.67 GW/m²K so that G_{Parallel} is 3.67 GW/m²K. The SBM result is 3.38 ± 0.30 GW/m²K, giving a \( \Delta G_{Interaction} \) of –0.29 GW/m²K. For the Type IVA-2 junction, G_{Top} is again 3.67 GW/m²K, while G_{Bottom} is 5.87 GW/m²K [representing the phonon radiation limit, i.e., when all \( \alpha \) in Eq. (1) are unity]. G_{Parallel} is then 4.77 GW/m²K, while the SBM result is 4.31 ± 0.39 GW/m²K, giving a \( \Delta G_{Interaction} \) of –0.46 GW/m²K. Unlike in bilayer graphene, where the
addition of a second layer reduces the thermal conductivity by nearly an order of magnitude\(^\text{12,13}\), the addition of a second layer reduces the thermal conductance of graphene/hBN interfaces by less than 10%.

The effect of the interlayer interaction can be understood by considering the modal transmission coefficients as a function of frequency for the single-layer and bilayer systems, as plotted in Figs. 6(a)–6(c). For the single layer, Fig. 6(a), the transmission coefficients for incident phonon modes normal to the interface converge to 0.99 at a low frequency. This value matches the prediction of the acoustic mismatch model and is so close to unity because graphene and hBN have almost identical unit cell masses and sound speeds. Aside from the doubling of the number of modes from a single-layer to a bilayer system, the transmission coefficient plots for Type IIA and Type IVA-1 junctions are nearly indistinguishable. The most notable differences are the reduced transmission coefficients near 50 Trad/s and in the region 250–300 Trad/s in the Type IVA-1 junction. In the Type IVA-2 junction, the transmission coefficients shown in Fig. 6(c) can be decomposed to those in the range of 0.5 to 1, where the profile closely replicates that of the Type IIA system, and those in the range of 0 to 0.5, where the great number of modes at 0.5 suggests a similarity to single-layer graphene, where all transmission coefficients are unity. These qualitative similarities suggest that many modes are largely unaffected by the interlayer interaction. This is not the case for all modes, the most obvious of which are the modes with transmission coefficients that lie between 0 and 0.5. Since they do not fit either the Type IIA profile or the single-layer graphene profile, they are influenced by the bilayer interaction in a non-trivial manner. It is the reduction in the transmission coefficient of these modes that create a negative \(\Delta G_{\text{Interaction}}\). The limitation of \(\Delta G_{\text{Interaction}}\) to only 10% of the single-layer value can be attributed to the weakness of the van der Waals interlayer interaction.

The Type II-S junctions, where the substrate is modeled by an on-site potential, represent a simpler computational approach for capturing the bilayer interaction. The thermal conductances of the substrated Type IIA-S junction are 3.16 ± 0.13 GW/m\(^2\)K, a decrease of 0.51 GW/m\(^2\)K from the monolayer Type IIA junction of 15%. This reduction is similar to the 0.46 GW/m\(^2\)K reduction for the Type IVA-2 explicit bilayer junction. Two-thirds of the decrease in the substrated system comes from the contributions of the OP modes. The primary effect of the substrate interaction is to lift the ZA branch from 0 to 25 Trad/s at the \(\Gamma\) point so that these modes are less populated. Accompanied with this change is a reduction of \(v_{g,x}\) of the ZA branch from \(\Gamma\) to K and \(\Gamma\) to M. A similar effect is seen in the explicitly modeled bilayer systems, where the second layer lifts the ZA branch from 0 to 18 Trad/s at the \(\Gamma\) point.\(^\text{11}\) Indeed, the change in the ZA branch is the only major alteration to the dispersion when a second layer of either graphene/hBN (Type IVA-1) or graphene (Type IVA-2) is added. The accuracy of the simple substrate model lies in its ability to capture this change in the dispersion.

**IV. SUMMARY**

Using the SBM to compute mode-resolved transmission coefficients, we found that the primary contributors to the thermal conductance of graphene/hBN heterostructures are acoustic phonon modes with frequencies below 100 Trad/s. These modes have high group velocity, high population, and transmission coefficients near unity [see Figs. 4(a) and 4(b)]. The use of an accurate cross-interface interaction and quantum statistics dramatically impacts the interface thermal conductance.

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**FIG. 6.** Modal transmission coefficient versus frequency for the (a) Type IIA, (b) Type IVA-1, and (c) Type IVA-2 junctions and their corresponding thermal conductances as calculated from the SBM.
conductance. Ignoring the former increases the prediction by a factor of 1.5, while ignoring the latter increases it threefold. The thermal conductances of the isolated armchair and zig-zag graphene/hBN interfaces correspond to a Kapitza length of 700 nm of single-layer graphene based on a thermal conductivity of 2600 W/m K. While the thermal resistance of such interfaces is significant compared to bulk graphene, the thermal conductances are one to two orders of magnitude larger than typical interface conductances in three-dimensional materials, which range from tens to hundreds of MW/m K.  

The thermal conductance of a finite graphene/hBN superlattice junction depends on the superlattice length and the lead species. As shown in Fig. 5, junctions with matched graphene/graphene leads have a 5% to 10% greater thermal conductance than comparable junctions with mismatched graphene/hBN leads. This difference is a result of transmission that occurs in the matched lead case but cannot occur in the mismatched lead case due to the hBN bandgap. This lead effect is a consequence of our assumption of harmonic interactions, but because the Debye temperatures of both graphene and hBN are high, such behavior may be observable at room temperature.

Finally, we found that the thermal conductances of explicitly modeled bilayer junctions of graphene/hBN do not differ greatly from those predicted from simpler models (e.g., an independent parallel transport model or a single-layer with an on-site potential). The strength of the intralayer van der Waals interaction is not strong enough to cause a significant coupling between the layers. Since the intralayer interactions are far softer than the in-layer interactions, however, anharmonic effects could be significant at room temperature, which may increase the thermal conductance of a real bilayer junction.

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APPENDIX A: SCATTERING BOUNDARY METHOD

The scattering boundary method (SBM) is a method to compute the transmission coefficient \( \alpha(\mathbf{k}, \nu) \) of the phonon mode \( \langle \mathbf{k}, \nu \rangle \) across a junction, where \( \mathbf{k} \) denotes the wavevector and \( \nu \) denotes the polarization. It is a lattice-dynamics method that was first formulated by Lumpkin et al. as an analytical solution to an interface between two one-dimensional chains. This formalism was extended to two dimensions by Young and Maris and to three dimensions by Zhao and Freund. It has since been applied to silicon/germania and Lennard-Jones systems. The SBM is theoretically equivalent to the atomistic Green’s function method.

The SBM computational domain, shown in Fig. 7, is built from an atomistically defined junction and left and right boundaries, which represent semi-infinite leads. The required inputs to the SBM are the bulk phonon modes of the left and right leads, the atomic structure of the junction, and the second-order (i.e., harmonic) force constants between the atoms within the junction. The formulation presented here is applicable to one-, two-, and three-dimensional systems.

The SBM computes \( \alpha(\mathbf{k}, \nu) \) by solving Newton’s second law of motion in the steady state when the phonon mode \( \langle \mathbf{k}, \nu \rangle \) is incident on the junction from the left boundary. The phonon modes are treated as plane waves and, because all interactions are harmonic, the entire system evolves at \( \omega(\mathbf{k}, \nu) \), the frequency of the incident phonon.

For every atom within the junction, the equations to be solved are

\[
-\omega^2(\mathbf{k}, \nu) m^j \ddot{x}^j_0 = \sum_{\beta \neq \delta} \Phi^j_{\alpha \beta} \dot{x}^\beta_0,
\]

where \( m^j \) is the mass of atom \( i \), the unknown \( x^j_0 \) is the \( j \)th Cartesian degree of freedom of atom \( i \), and \( \Phi^j_{\alpha \beta} \) is the second-order force constant between the \( j \)th Cartesian degree of freedom of atom \( i \) and the \( \beta \)th Cartesian degree of freedom of atom \( j \). The summation is over all atoms and their degrees of freedom both in the junction and in the boundaries, including self-interaction terms involving the off-diagonal force constant elements \( \Phi^j_{\alpha \beta} \).

For all atoms in the left boundary, the equations of motion differ from those in the junction. The unknown atomic degrees of freedom \( x^j_z \) for atoms that interact with the junction are prescribed by

\[
x^j_z = e(\mathbf{k}, \nu)^j_z + \sum_{\kappa, \nu'} E(\mathbf{k'}, \nu') \delta(\omega(\mathbf{k}, \nu) - \omega(\mathbf{k'}, \nu')).
\]

FIG. 7. Schematic representation of the SBM computational cell for an armchair interface indicating the left boundary (red) and the right boundary (blue).

Here, \( e(\mathbf{k}, \nu)^j_z \) is the eigenvector component of phonon mode \( \langle \mathbf{k}, \nu \rangle \) corresponding to the \( j \)th Cartesian degree of freedom of atom \( i \). The first term on the right hand side represents the incident phonon mode. Without loss of generality, it is given unit amplitude. The second term on the right hand side represents a superposition of reflected phonon modes, where the summation is performed over the phonon modes of the left lead. The delta function indicates that only reflected modes with the same frequency as the incident mode are considered. The amplitudes of the reflected waves, \( r(\mathbf{k'}, \nu') \), are unknown.
For all atoms in the right boundary, the unknown atomic degrees of freedom $x^j_x$ for atoms that interact with the junction are prescribed by

$$x^j_x = \sum_{k, \nu} t\left(k', \nu' \right) e^{i\left(k, \nu \right) \cdot x^j_x} \delta\left[\omega\left(k, \nu\right) - \omega\left(k', \nu'\right)\right].$$

(A3)

Since the right boundary contains only transmitted modes, the summation is performed over the phonon modes of the right lead and the unknowns $t\left(k', \nu' \right)$ are the amplitudes of the transmitted waves.

Equations (A1)–(A3) form a linear system of equations of the form $Ax = b$ that can be solved for the unknowns $x^j_x$, $r\left(k', \nu' \right)$, and $t\left(k', \nu' \right)$. The transmission coefficient $x\left(k, \nu\right)$ can then be computed via

$$x\left(k, \nu\right) = \frac{1}{R} \sum_{k, \nu} \left[|t\left(k', \nu' \right)|^2 v_{g,k}\left(k', \nu' \right) \delta\left[\omega\left(k, \nu\right) - \omega\left(k', \nu'\right)\right]\right],$$

(A4)

where $v_{g,k}$ is the phonon mode group velocity in the cross-junction direction. The size of the boundaries should be chosen to contain enough atoms so that the system is at least exactly solvable (i.e., $A$ is square). That is, the number of degrees of freedom within the left (right) boundary should coincide with the number of modes summed over in Eq. (A2) [(A3)].

For reliability, we recommend that a buffer region be made between the boundaries and the junction. All atoms within the left (right) buffer region are then subject to both Eqs. (A1) and (A2) [(A3)]. The addition of the buffer region creates an overdetermined system (i.e., $A$ has more rows than columns) that can be solved using singular value decomposition (SVD).

APPENDIX B: REDUCTION OF SCATTERED MODE NUMBER

1. Motivation

Within the scattering boundary method (SBM), the equations of motion within the left and right boundaries are given in Eqs. (A2) and (A3). The summations over the reflected and transmitted modes are performed over the first Brillouin zones of their respective leads. A numerical solution of these equations would require meshing and summing over a large number of wavevectors and representing the Dirac delta functions as narrow Gaussians. The computational load can be decreased by reducing the number of wavevectors considered to those that (i) satisfy the appropriate geometric condition and (ii) satisfy the frequency constraint imposed by the delta functions. The implementation of these conditions is discussed in Secs. B2 and B3.

2. Wavevector condition

The perfect interface between two leads shown in Fig. 7 is aperiodic in the cross-interface $x$-direction, but remains periodic in the $y$-direction along the interface (and the $z$-direction for a three-dimensional system). Whether or not the $y$- and $z$-periods of the interface match the corresponding bulk periods depends on the interface being studied. Note that the following discussion pertains only to two- and three-dimensional systems, as the wavevector condition is trivial in one-dimension.

In the event that the interface periods match those of the bulk leads, scattering is specular and

$$k_y\left(k', \nu' \right) = k_y\left(k, \nu\right),$$

(B1)

$$k_z\left(k', \nu' \right) = k_z\left(k, \nu\right).$$

(B2)

That is, all scattered phonon modes have the same wavevector components along the interface as the incident mode.

In the event that the interface periods are larger than those of the bulk (the case for all junctions considered in this work), Eqs. (B1) and (B2) are modified to

$$k_y\left(k', \nu' \right) \equiv k_y\left(k, \nu\right) \mod 2\pi/a_{\text{int},y},$$

(B3)

$$k_z\left(k', \nu' \right) \equiv k_z\left(k, \nu\right) \mod 2\pi/a_{\text{int},z},$$

(B4)

where $a_{\text{int},y}$ ($a_{\text{int},z}$) is the interface $y$-period ($z$-period). Consideration of a larger unit cell also allows for the inclusion of roughness at the interface. Whereas the conditions given in Eqs. (B1) and (B2) lead to only two planes of constant $k_y$ and $k_z$ within the first Brillouin zone upon which scattering might occur, Eqs. (B3) and (B4) lead to many, whose number increases as $a_{\text{int},y}$ and $a_{\text{int},z}$ increase. As $a_{\text{int},y}$ and $a_{\text{int},z}$ go to infinity (as would be required for a rough interface), all wavevectors are possible and scattering is diffuse. Within the context of graphene/hBN, where the Brillouin zone is two-dimensional, only the first condition [Eq. (B3)] is considered.

3. Frequency condition

After consideration of the wavevector condition, the possible scattered modes are reduced to those that lie along certain planes of constant $k_y$ and $k_z$. The next step is to select the modes from each plane that have frequency $\omega\left(k, \nu\right)$.

The first step is to find the $k_z$’s at a given $k_y$ and $k_z$ that have a mode at frequency $\omega\left(k, \nu\right)$. Let $D$ be the bulk dynamical matrix associated with the lead in question. The dependence of $D$ on $k_z$ is isolated by decomposing $D$ into segments corresponding to the period in the $x$ direction, $a_x$,

$$D\left(k\right) = D_{-N} e^{-iNk\cdot a_x} + \cdots + D_{-1} e^{-ik\cdot a_x} + D_0 + D_{+1} e^{iNk\cdot a_x} + \cdots + D_{+N} e^{iNk\cdot a_x}. $$

(B5)

There are $N$ unit cell replications in the $-x$ and $+x$ directions relative to the central unit cell. With this decomposition, $D_{-j}$ and $D_{+j}$ depend only on $k_y$ and $k_z$. All dependence on $k_z$ is in the complex phase factors. Now treat $k_z$ as an unknown parameter and rewrite the harmonic lattice dynamics problem as...
Here, \( \mathbf{0} \) and \( \mathbf{I} \) represent zero and identity matrices of the same dimension as \( \mathbf{D} \), blanks are zeros, and \( \mathbf{e} \) is the harmonic lattice dynamics polarization eigenvector of the as yet unknown matching mode. Eq. (B6) is a generalized eigenvalue problem with eigenvectors \( \mathbf{v} \) and eigenvalues \( \xi \). Once the eigenvalues \( \xi \) are found, \( \kappa_x \) can be determined via

\[
\kappa_x = -i \log(\xi) / \alpha_x
\]

This process is repeated for all planes of constant \( \kappa_y \) and \( \kappa_z \) until a complete list of reflected and transmitted modes is formed. Once this list is formed, Eqs. (A2) and (A3) are simplified to

\[
x_x^j = e(\kappa_x, \nu_x^j) + \sum_{\rho} \mathbf{r}_\rho \mathbf{e}^{(\kappa_x', \nu_x^j)}_{x, \rho}
\]

and

\[
x_x^j = \sum_{\tau} \mathbf{r}_\tau \mathbf{e}^{(\kappa_x', \nu_x^j)}_{x, \tau}
\]

where \( \rho \) and \( \tau \) index over the reflected and transmitted mode lists.

REFERENCES