Interplay between total thickness and period thickness in the phonon thermal conductivity of superlattices from the nanoscale to the microscale: Coherent versus incoherent phonon transport

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This document contains details on sample growth, time domain thermoreflectance (TDTR), thermal conductivity data and experimental data analysis, Atomistic Green’s function analysis of coherent transport and incoherent transport at mixed interfaces, density functional theory applied to GaAs and AlAs, and modeling the spectral phonon contributions to the thermal conductivity in AlAl-GaAs superlattice.

1 Sample Growth

The samples were grown on epi-ready GaAs (001) substrates in a VG V80 molecular beam epitaxy (MBE) reactor. The substrate temperature is measured using an optical pyrometer. Prior to growth, the native oxide on the substrates is desorbed at 630 °C for 20 minutes. The substrate temperature is then brought down to 580 °C and a GaAs smoothing layer of thickness $d_{\text{smooth}}$ is grown. Reflection High-Energy Electron Diffraction (RHEED) transforms from a spotty pattern (indicating desorption of native oxide) to a clear streaky $2\times4$, showing the growth of As-stabilized smooth GaAs surface. Following this, with an As overpressure, the Al and Ga shutters are alternated based on the period thickness for the growth of the superlattice at 580 °C. A similar growth temperature is used for the growth of the GaAs thin film samples. The AlAs and GaAs growth rates (calibrated by RHEED oscillations) are kept constant at 0.3 ML s$^{-1}$. A V/III ratio of 13 is maintained between As and Ga across the SL samples growth as measured by an ionization gauge.

Supplemental Fig. 1 shows the schematic of the structure of the AlAs-GaAs SLs. Supplemental Table 1 lists the structural and growth parameters of all tested samples along with the thermal conductivity measurement results at room temperature. For the 2 nm period thickness set, a 5 nm GaAs cap layer was grown on top to prevent oxidation of Al inside AlAs prior to coating the samples with aluminum.

2 Time-Domain Thermoreflectance (TDTR)

We use a double color TDTR setup with pulsed laser output at 80 MHz repetition rate, 800 nm central wavelength, and pulse widths of 100 fs at the output of the laser cavity. The pump beam is converted into 400 nm light through a BIBO crystal. The probe is delayed by a mechanical delay stage up to 5.5 ns. Both the pump and probe are coaxially focused on the sample down to Gaussian $1/e^2$ radii.
Supplemental Figure 1: A schematic showing the AlAs-GaAs SLs structure. For the 2 nm period thickness set, a 5 nm GaAs cap layer was grown on top to prevent oxidation of Al inside AlAs prior to coating the samples with aluminum. (right) A schematic of the AlAs-GaAs SL structure simulated using Green’s functions.

of 25 and 10 $\mu$m, respectively. We monitor the ratio of in-phase to out-of-phase components of the lock-in amplifier signal as a function of the time delay. The lock-in amplifier signal is fit to a multilayer thermal model in which the thermal conductivity of the SL film and the interface conductance between the aluminum coating and film are the free parameters [1, 2, 3]. TDTR measurements were done at 3 different modulation frequencies (3.5, 8.8 and 12.2 MHz) where at least five measurements were conducted at each frequency. The average of all these measurements is reported. The thermal conductivities of the GaAs substrate and 200 nm GaAs smoothing layer are measured separately from an identical GaAs substrate and 200 nm GaAs film grown under the same conditions used for the SL films.

The thermal interface conductance between the SL film or GaAs thin film and the buffer-substrate layer is found to be high enough that we are completely insensitive to it. This is justified by the values of $h_K$ shown in Supplemental Fig. 2 (derived from a series resistor model from the thermal conductivity data and number of interfaces per unit length of the SL; see Eq. 2 and discussion in Section 5 of
Supplemental Table 1: period thickness, $d_{SL}$, thickness, $L$, smoothing layer thickness, $d_{smooth}$, cap layer thickness, $d_{cap}$, and thermal conductivity at room temperature of AlAs-GaAs superlattices and GaAs thin films.

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<th>Sample Code</th>
<th>$d_{SL}$ (nm)</th>
<th>$L$ (nm)</th>
<th>$d_{smooth}$ (nm)</th>
<th>$d_{cap}$</th>
<th>$\kappa_{300K}$ (W m$^{-1}$ K$^{-1}$)</th>
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GaAs thin films:

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<th>$d_{smooth}$ (nm)</th>
<th>$d_{cap}$</th>
<th>$\kappa_{300K}$ (W m$^{-1}$ K$^{-1}$)</th>
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<td>2,160</td>
<td>200</td>
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<td>34.0 ± 3.4</td>
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Supplemental Figure 2: Derived thermal boundary conductance in the AlAs-GaAs SLs as a function of period thickness.

this Supplemental Material), where the data start to level off at the 12 nm period, and thus one may expect that $h_K$ for a single AlAs-GaAs interface will be extremely high. A value higher than 200 MW m$^{-2}$ K$^{-1}$ for the interface conductance between the SL film (where the bottom layer of the SL film is AlAs, see Supplemental Fig. 1) and the GaAs smoothing layer is enough to make the TDTR measurement completely insensitive to this parameter. Note, the increase in $h_K$ with the decrease in $d_{SL}$ suggests that in shorter $d_{SL}$, a larger portion of the phonon spectrum ballistically traverse the AlAs-GaAs samples scattering less frequently at the internal interfaces defining the SL periodicity, as we have discussed previously. This result has been shown in Si-Ge, AlN-GaN, as well as AlAs-GaAs SLs previously [4]. However, the large interface density in SLs with shorter $d_{SL}$ leads to a higher thermal resistance that suppresses the thermal conductivity of the 2 nm period thickness samples well below that of 12 and 24 nm samples. Even with the high values of $h_K$ (1.7 - 4.1 GW m$^{-2}$ K$^{-1}$) the thermal conductivities of the SLs are significantly lower than that of $\kappa_0$, demonstrating that although the trend in thermal conductivity is dictated by long-range boundary scattering, scattering of short mfp phonons from internal interfaces can significantly impact the magnitude of thermal conductivity.
Supplemental Figure 3: Total SL resistance, $R$, as a function of total SL thickness, $L$, for the $d_{SL} = 2$, 12, and 24 nm period samples. We calculate $R$ as $R = L/\kappa$, where $\kappa$ is the SL thermal conductivity measured via TDTR.

of SLs.

The trend in Supplemental Fig. 2 suggests that this value is appreciably higher than $\sim 200$ MW m$^{-2}$ K$^{-1}$. In the analysis of TDTR data of thick films, we use a three layer model where the layers are: Aluminum coating, SL film or GaAs thin film, and smoothing-substrate layer. For films with thicknesses less than 60 nm we use a two-layer model and determine the effective thermal conductivity of the SL or GaAs film from the interface conductance. The best fit value from a two layer model is then compared to the result from a three layer model. We found that the effective thermal conductivity from two-layer model agrees to within 15% with the result from a three-layer model for the three different measurement frequencies. We report the average of the results obtained via these two approaches. In the main document Fig. 2C, we show trends in the thermal conductivity that demonstrate a transition from ballistic to diffusive behavior in the superlattices when the total thickness of the superlattices decrease below $\sim 200$ nm, regardless of period thickness. As an additional means of recognizing this ballistic-to-diffusive cross over and further supporting this conclusion, we plot the total thermal resistance, $R = L/\kappa$, of the superlattice as a function of total superlattice thickness, $L$, shown in Supplemental
Fig. 3. If the thermal conductivity of the superlattices were purely diffusive, we would expect a linear trend over all SL thicknesses. The clear discontinuity in the slope of $R(L)$ vs. $L$ around $L \sim 200$ nm indicates a ballistic-to-diffusive crossover around this total superlattice length, also mentioned in the main document. In a purely diffusive transport situation, the intercept $R(L = 0)$ would correspond to the thermal boundary resistance ($h_K = 1/R(L = 0)$). Extrapolating the resistances for $R(L > 200$ nm), which are thermal conductivities in the diffusive regime, to $R(L = 0)$ yields values of $h_K = 1/R(L = 0) > 200$ MW m$^{-2}$ K$^{-1}$ for all periods, consistent with our discussion above regarding our ability to separate the intrinsic thermal conductivity and thermal boundary conductances of the SLs. Furthermore, note that in the ballistic limit, all resistances converge to a similar value for $R$ as $R$ approaches $L = 0$. This indicates that there are negligible differences in the thermal boundary conductances among the different samples, suggesting that the differences in the measured thermal conductivities in the SL samples with different $d_{SL}$ at a given $L$ is not due to any differences in contacts/thermal boundary conductances, and indeed representative of differences in the intrinsic thermal conductivities of the SLs.

3 Superlattice conductance in the coherent limit

In the harmonic limit, the thermal conductance across a system in between two contacts can be calculated using non-equilibrium Green’s function formalism as [5, 6, 7]

$$G = \int_0^\infty \frac{d\omega}{2\pi} \hbar \omega \frac{\partial f}{\partial T} \text{Trace}\{\Gamma_l G \Gamma_r G^\dagger\},$$

(1)

where $\hbar \omega$ is the phonon energy, $f$ is the Bose-Einstein distribution, $T$ is the temperature, $G$ is the retarded Green’s function for the system and $\Gamma_i$ is the anti-hermitian part of the self-energy matrix that describes the interaction of the system with contact $i$. The Green’s function formalism solves exactly the equation of motion of the system connected with infinite contacts and accounts for the resonances and anti-resonances forming from interference. In this way, the method captures coherent effects like the formation of minibands in superlattices. In this Green’s function formalism, the sum of all the transmissions over all phonon modes from a left-contact to a right-contact is denoted as $MT$, where $MT = \text{Trace}\{\Gamma_l G \Gamma_r G^\dagger\}$, with $G$ the retarded Green’s function for the system and $\Gamma_i$ the anti-hermitian part of the self-energy matrix that describes the interaction of the system with contact $i$. 
Note, since $MT$ is a transmission summed over all available phonon modes, this number is not constrained to a maximal value of unity.

For the Green’s function simulations, we try to replicate the SL samples measured using TDTR, which are GaAs-AlAs periods sandwiched between GaAs films (Supplemental Fig. 1). The value of thermal conductivity extracted from the TDTR measurements and fitting process does not have contributions from the Aluminum layer or Aluminum-GaAs interface, as we discussed above. Also, note all SL samples are terminated with the GaAs layer. If we change one of the contacts on our Green’s function simulations to Al, we will change the spectral distribution of phonons on that contact as well as the transmission from the contact to the SL. These two modifications will change the shape of $MT$ vs. frequency to reflect the available transport channels in Al and will shift $MT$ downwards due to the reflection at the Al-GaAs interface. Those modifications will add a constant resistance to all of our calculation and thus the trends presented in Figs. 2 and 3 of the main document should remain the same but will shift vertically.

For the conductance calculations, we assume that AlAs has the same lattice constant and interatomic force constants as those of GaAs. This changes some frequencies of the AlAs dispersion up to 5% (Supplemental Fig. 4). We neglect the LO-TO splitting and assume that the interfaces between AlAs and GaAs are perfectly abrupt and defect-free. Those assumptions facilitate the calculations while showing the trend of the superlattice conductance vs. period in the purely coherent limit. We use GaAs for the left and right contacts of the calculation.

The 2nd order interatomic force constants are obtained from a plane wave DFT solver Quantum Espresso (QE) [8, 9]. The 2nd order force constants are calculated by Density Functional Perturbation Theory (DFPT) method in QE with $5 \times 5 \times 5$ Brillouin Zone mesh, which corresponds to an interaction range up to the 2nd neighbor unit cell. In the calculation, a plane wave self-consistent calculation of the ground state is first done with norm-conserving pseudopotentials with Perdew-Zunger LDA exchange-correlation functionals based on the Von Barth-Car Method. The system converges by a cutoff energy of 30 Rydberg with a $8 \times 8 \times 8$ Monkhorst Brillouin Zone grid. As shown in Supplemental Fig. 4, the 2nd order harmonic force constants generate dispersions of GaAs and AlAs that agree well with experimental data, which confirms the validity of the parameters we employ. [8, 9].
4 Superlattice conductance with interface mixing

Phonon transport is purely coherent for the SL with perfect interfaces due to the construction of the GF method as described in previous section. Interatomic mixing at the interfaces, however, will contribute to spatial incoherence by randomizing the phase of the phonons through several sequences of independent scattering events. Note that there is a subtlety here. A particular distribution of interfacial disorder still keeps the overall phonon transport coherent, by shifting the phases by a determined amount (much like we how interference with a split ring is still observed even in presence of static impurities). However, repeating the experiment with several random distributions, or equivalently, redoing our GF calculations with several independent SLs containing different random mixing amounts, and directly averaging their transmissions (i.e., adding probabilities instead of probability amplitudes), leading to the capture of spatial incoherence in the system.

In our interface mixing simulations, we prescribed the mixing for one unit cell at each side of the interface, which accounts for about 1 nm random shuffling of Ga and Al atoms at each interface. This structural setup agrees with our the degree of mixing in our samples, as observed in the STEM images. Note that the 2 nm SLs still demonstrate superlattice structures instead of complete mixing (alloy), so in our simulations, we also only set up the mixing percentage less than 50%. Those mixing unit cells adjacent to the interfaces in GaAs have 20% chance of Ga atoms being replaced by Al atoms; similarly, those mixing unit cells adjacent to the interfaces in AlAs have 20% chance of Al atoms being replaced by Ga atoms. To
Supplemental Figure 5: (A) $MT$ per perpendicular unit cell for SL with interatomic mixing at the interfaces. (B) $MT$ per perpendicular unit cell for SL with perfect interfaces

take into account enough random nature in the chemical order, the cross-section area size is $3 \times 3$ of the primitive unit cell cross-section area size. The wavevector sample for the cross-section Brillouin Zone is $20 \times 20$, which is carefully chosen to satisfy the conductance convergence. Other setups are the same as the coherent transport simulations. We performed the interface mixing simulations for 2 nm, 12 nm and 24 nm period SLs with the total length, $L$, up to 768 nm, 768 nm and 1152 nm, respectively (the corresponding number of periods is 384, 64, 48 for each set, respectively), and each simulation is repeated three times to obtain an averaged transmission to capture the incoherent behavior.

In Supplemental Fig. 5, we plot $MT$ as a function of phonon angular frequency, $\omega$, simulated for selected SLs with various period thicknesses ($d_{SL} = 2$, 12 and 24 nm) for two different thicknesses (total number of periods of 2 or 12 for each $d_{SL}$ case). These correspond to the superlattice thicknesses, $L$, in the legend of Supplemental Fig. 5. Note, $MT$ is sum of all transmission of each phonon at any given frequency traversing from left to right contact. Supplemental Fig. 5(A) shows $MT$ calculations for the case of mixed interfaces in the AlAs-GaAs SL, where Supplemental Fig. 5(B) shows the results for the smooth interface case. Note, more formally, $MT = \text{Trace}\{\Gamma_lGT_rG^\dagger\}$, with $G$ the retarded Green’s function for the system and $\Gamma_i$ the anti-hermitian part of the self-energy matrix that describes the interaction of the system with contact $i$, as described in the main document.
In the case of mixed interfaces, the total transmission for the 12 and 24 nm periods is the same when the number of periods of the sample is the same. This result follows from the lack of scattering between interfaces in our simulations. This result should be valid for samples where phonon-phonon interactions are not the dominant scattering process. Our experimental data confirms this result for samples shorter than 100 nm as the conductance of the 24 nm and 12 nm period samples, derived from experiments, follows a single curve (Fig. 2c in the main document). When the period of the SL is decreased to 2 nm, $M_T$ increases, which corresponds to the increase in the calculated conductance (and we ascribe to the trend in the conductance derived from our experimental data, as discussed in the main document). In our simulations, we hypothesize that this increase in $M_T$ and conductance results from the transition from a SL of single crystalline AlAs and GaAs and an alloy, since the 2 nm period SL contains random interatomic mixing that can account for 50% of the volume, on average. We discard the increase being the result of coherent miniband formation, since if that were the case, we would expect similar features for the $M_T$ of the SL with and without interatomic mixing at the interfaces, which is not the case when comparing Supplemental Fig. 5(A) and (B).

Even in the absence of phonon-phonon interactions, when random interatomic mixing is added at the interfaces, each interface brings about some incoherence to the transport process. Therefore, incoherent phonon transport becomes increasingly important as the number of interfaces increases. Our simulations show that $M_T$ decreases as the number of periods increases Supplemental Fig. 5(A), which implies that phonon transmission and conductance decreases as the number of periods increases. Note, the constant $M_T$ regardless of the periodicity for any given number of periods is only observed in the case of smooth interfaces (perfectly atomically abrupt with no interfacial mixing), as shown in Supplemental Fig. 5(B). Only in this case of atomically smooth AlAs-GaAs interfaces comprising the SL periods can coherent transport be a dominant contributor to thermal conductivity of SLs.

Direct comparison of our Green’s function calculations with the experimental data is difficult because our calculations do not include contributions from phonon-phonon scattering. Also, in our Green’s function calculations, we assume that the interatomic force constants (IFCs) are fixed. However, the IFCs of GaAs and AlAs are different and more importantly, the IFCs at the interfaces might differ from the those of pure GaAs and AlAs. Including those changes in the calculation will most likely decrease the conductance at each interface and hence the conductance of the
In spite of our assumptions, our model captures the spatial incoherence brought about by the randomness of the interatomic mixing at each interface, which is the base of our conclusions.

5 Modeling the spectral phonon contributions to the thermal conductivity in AlAs-GaAs superlattices

To gain insight into the spectral distribution of phonons that contributes to the thermal conductivity of the AlAs-GaAs, we model the thermal conductivity of the SLs using a series resistor approach. We separate the thermal conductivity into contributions from long and short range boundary scattering, so that the SL thermal conductivity, \( \kappa_{SL} \), is given by:

\[
\frac{L}{\kappa_{SL}(L,d_{SL},T)} = \frac{L}{\kappa_{HSL}(L,T)} + \frac{2L}{d_{SL}h_K(d_{SL},T)}
\]

where \( h_K \) is the thermal boundary conductance across the AlAs-GaAs interfaces and is varied to fit the data to the model for \( L > 200 \) nm and \( \kappa_{HSL} \) is the thermal conductivity of a hypothetical SL (HSL) of thickness \( L \) sans interface scattering (thus, assuming no interface resistance/infinite thermal boundary conductances at the AlAs-GaAs interfaces). We model \( \kappa_{HSL} \) using a Holland/Callway-type model where we use average properties of GaAs and AlAs (lattice constant, dispersion curves, and scattering times) [10, 11]. This is justified by the fact that long mfp phonons see the SL as a homogeneous material without discrete interfaces. We account for the \( L \) dependence by including a boundary scattering term into the calculation of \( \kappa_{HSL} \). In this model, \( \kappa_{HSL} \) accounts for the long range boundary scattering and \( h_K \) accounts for the short range boundary scattering.

Before delving into the details of our calculation and analysis of \( \kappa_{HSL} \), we briefly discuss the implications of the trends in \( h_K \) vs. \( d_{SL} \) presented earlier in Supplemental Fig. 2. The increase in \( h_K \) with the decrease in \( d_{SL} \) suggests that in shorter \( d_{SL} \), a larger portion of the phonon spectrum ballistically traverse the AlAs-GaAs samples scattering less frequently at the internal interfaces defining the SL periodicity, as we have discussed previously. This result has been shown in Si-Ge, AlN-GaN, as well as AlAs-GaAs SLs previously [4]. However, the large interface density in SLs with shorter \( d_{SL} \) leads to a higher thermal resistance that suppresses the thermal conductivity of the 2 nm period thickness samples well below that of 12 and 24 nm samples. Even with the high values of \( h_K \) (1.7 - 4.1 GW m\(^{-2}\) K\(^{-1}\)) the thermal
conductivities of the SLs are significantly lower than that of $\kappa_{\text{HSL}}$, demonstrating that although the trend in thermal conductivity is dictated by long-range boundary scattering, scattering of short mfp phonons from internal interfaces can significantly impact the magnitude of thermal conductivity of SLs.

We calculate the thermal conductivity of the hypothetical “interface-less” superlattices ($\kappa_{\text{HSL}}$ via:

$$\kappa_{\text{HSL}}(L, T) = \frac{1}{3} \sum_j \int_0^{\omega_{c,\text{SL},j}} C_{\text{SL},j}(T, \omega) \nu_{\text{SL},j}^2(\omega) \tau_{\text{SL},j}(\omega, L, T) \, d\omega$$  \hspace{1cm} (3)

where $j$ is the phonon branch (LA and TA) and $\nu_{\text{SL},j}$ is the slope of the SL dispersion curve shown in Supplemental Fig. 4. The integration is carried over the frequencies given by the SL dispersion and $\omega_{c,\text{SL},j}$ is cutoff frequency in this dispersion. For this Holland/Callaway approach to modeling $\kappa_{\text{HSL}}$, we assume isotropy in GaAs and AlAs and use the phonon dispersions in the $\Gamma \rightarrow X$ directions of the respective materials. $C_{\text{SL},j} = \hbar \omega D_j(\omega) \partial f / \partial T$ is the heat capacity of the SL using the average dispersion curve, where $D_j(\omega) = \omega^2/[2\pi^2 \nu_{\text{SL},j}^2(\omega)]$ is the density of states and $f$ is the Bose-Einstein distribution. The relaxation time for a given frequency, temperature, thickness, and branch, $\tau_{\text{SL},j}(\omega, L, T)$, is related to the individual scattering processes via Matthiessen’s rule, $\tau_j = (\tau_{-1, U,j} + \tau_{-1, I,j} + \tau_{-1, L,j})^{-1}$, where $\tau_U$, $\tau_I$, and $\tau_L$ are the Umklapp, impurity, and boundary scattering times, respectively. These are given by:

$$\tau_{-1, U,j}(\omega, T) = \frac{1}{2} \tau_{-1, U,j,\text{AlAs}}(\omega, T) + \frac{1}{2} \tau_{-1, U,j,\text{GaAs}}(\omega, T)$$ \hspace{1cm} (4)

$$\tau_{-1, I,j}(\omega) = \frac{1}{2} \tau_{-1, I,j,\text{AlAs}}(\omega) + \frac{1}{2} \tau_{-1, I,j,\text{GaAs}}(\omega)$$ \hspace{1cm} (5)

and

$$\tau_{-1, j,L}(\omega, L) = \frac{\nu_{\text{SL},j}(\omega)}{L}$$ \hspace{1cm} (6)

where

$$\tau_{-1, U,j,\text{AlAs}} = B_{\text{AlAs}} \omega^2 T \exp(-C_{\text{AlAs}}/T)$$ \hspace{1cm} (7)

$$\tau_{-1, U,j,\text{GaAs}} = B_{\text{GaAs}} \omega^2 T \exp(-C_{\text{GaAs}}/T)$$ \hspace{1cm} (8)

$$\tau_{-1, I,j,\text{AlAs}} = A_{\text{AlAs}} \omega^4$$ \hspace{1cm} (9)

and

$$\tau_{-1, I,j,\text{GaAs}} = A_{\text{GaAs}} \omega^4$$ \hspace{1cm} (10)
Supplemental Figure 6: The agreement between the Kinetic Theory thermal conductivity model given by Supplemental Eq. 3 and the first principles calculations for thermal conductivity of AlAs and GaAs using the parameters listed in Supplemental Table 2.

Usually, the constants $A$, $B$, and $C$ are obtained by fitting data of bulk GaAs and AlAs thermal conductivity over temperature to a certain thermal conductivity model. However, to the best of our knowledge, no temperature dependent data on AlAs exist in the literature. In addition, there exists a huge disagreement in literature data on the thermal conductivity of GaAs. For instance, the room temperature value of the thermal conductivity of bulk, single crystalline GaAs is anywhere between 37 and 54.5 W m$^{-1}$ K$^{-1}$ (See page 47 in Ref. [12], also compare values between Refs. [13] and [14]). As a result, and to avoid this discrepancy and lack of data, we use the thermal conductivity of AlAs and GaAs from first principle calculations and fit these to a kinetic theory model similar to that given by Supplemental Eq. 3. In this case, the models for $\kappa_{GaAs}$ and $\kappa_{AlAs}$ are calculated using Supplemental Eq. 3 with the frequencies corresponding to that of GaAs and AlAs dispersion curves plotted in Supplemental Fig. 4, respectively. Supplemental Fig. 6 shows the agreement between first principles and the kinetic theory model.
Supplemental Table 2: Relaxation time parameters for AlAs and GaAs obtained by fitting the kinetic theory model for thermal conductivity given by Supplemental Eq. 3 to the first principle calculations.

<table>
<thead>
<tr>
<th>Material</th>
<th>$A$ (rad$^{-4}$ $s^3$)</th>
<th>$B$ (rad$^{-2}$ $s$ K$^{-1}$)</th>
<th>$C$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlAs</td>
<td>$7.8 \times 10^{-44}$</td>
<td>$2.00 \times 10^{-19}$</td>
<td>130</td>
</tr>
<tr>
<td>GaAs</td>
<td>$9.0 \times 10^{-44}$</td>
<td>$2.32 \times 10^{-19}$</td>
<td>90</td>
</tr>
</tbody>
</table>

for values of $A$, $B$, and $C$ listed in Supplemental Table 2.

For the first principle calculations, the thermal conductivities of GaAs and AlAs are calculated self-consistently by solving Boltzmann transport equation (BTE) with 2nd and 3rd order force constants. The thermal conductivities are calculated using the following equation [15]:

$$\kappa_{\alpha\beta} = \frac{1}{k_B T^2 \Omega N} \sum_\lambda f_0(f_0 + 1)(\hbar \omega_\lambda)^2 v^{\alpha}_{\lambda} F^\beta_{\lambda}.$$  \hspace{1cm} (11)

where $\Omega$ is the volume of the simulated unit cell, $N$ is the number of wavevectors $q$ used in the simulation, $f_0$ is the phonon occupation probability at the frequency $\omega$ and the simulated temperature following the Bose-Einstein distribution, $\hbar \omega_\lambda$ is the single phonon energy with normal mode $\lambda$ and $v^{\alpha}_{\lambda}$ is the projected velocity in the direction $\alpha$. All variables except $F^\beta_{\lambda}$ are calculated by lattice dynamics. $F^\beta_{\lambda}$, which has the dimension of mean free path, is solved self-consistently by using the following iterative loop [15, 16, 17, 18, 19]:

$$F_{\lambda} = \tau^0_{\lambda}(v_{\lambda} + \Delta_{\lambda}).$$  \hspace{1cm} (12)

$$\Delta_{\lambda} = \frac{1}{N} \sum_{\lambda',\lambda''}^{+} \Gamma_{\lambda\lambda'}^{\lambda''} (\xi_{\lambda\lambda''} F_{\lambda''} - \xi_{\lambda\lambda'} F_{\lambda'})$$

$$+ \frac{1}{N} \sum_{\lambda',\lambda''}^{-} \frac{1}{2} \Gamma_{\lambda\lambda'}^{\lambda''} (\xi_{\lambda\lambda''} F_{\lambda''} + \xi_{\lambda\lambda'} F_{\lambda'})$$

$$+ \frac{1}{N} \sum_{\lambda'} \Gamma_{\lambda\lambda'} \xi_{\lambda\lambda'} F_{\lambda'}.$$

In the iterative process, $\tau^0_{\lambda}$ is the total relaxation time from single mode relaxation time approximation (SMRTA), and its reciprocal is the single mode scattering rate.
Supplemental Figure 7: The thermal conductivities of GaAs and AlAs from the first principle calculation as compared to experimental data [10, 20]. The solid and dashed lines in this figure are identical to the data points shown in Supplemental Fig 6.

In this calculation, we account for anharmonicity and isotope scattering processes by Matthiessen’s rule. $\Gamma_{\lambda\lambda'}^{+\lambda''}$, $\Gamma_{\lambda\lambda'}^{-\lambda''}$ and $\Gamma_{\lambda\lambda'}$ are the scattering rates for three phonon absorption process, emission process, and isotope scattering process respectively. $\xi_{\lambda\lambda'}$ is defined as $\omega_{\lambda'}/\omega_{\lambda}$. The $\Delta_{\lambda}$ weights the deviation of the self-consistent process from the SMRTA, and adds a correction as the SMRTA incorrectly assumes that the normal scattering process results in thermal resistance [16, 17]. This calculation is done in an open source self-consistent BTE solver ShengBTE [15] with a dense $24 \times 24 \times 24$ q-mesh utilizing the first principle 2nd and 3rd force constants.

The thermal conductivities of GaAs and AlAs from first principles are replotted in Supplemental Fig. 7 showing a close match to available experimental results from Literature. The calculated scattering rates for GaAs and AlAs are plotted in Supplemental Fig. 8 and are in good agreement with previously reported results [21].

The 2nd order and 3rd order interatomic force constants are obtained from a
plane wave DFT solver Quantum Espresso(QE) [8, 9]. The 2\textsuperscript{nd} order force constants are calculated by Density Functional Perturbation Theory (DFPT) method in QE with $5 \times 5 \times 5$ Brillouin Zone mesh, which corresponds to an interaction range up to the 2\textsuperscript{nd} neighbor unit cell. In the calculation, a plane wave self-consistent calculation of the ground state is first done with norm-conserving pseudopotentials with Perdew-Zunger LDA exchange-correlation functionals based on the Von Barth-Car Method. The system converges by a cutoff energy of 30 Rydberg with a $8 \times 8 \times 8$ Monkhorst Brillouin Zone grid. The Born effective charges and dielectric tensors of the system are also calculated from the DFPT package to take the long-range Coulombic interactions into consideration. As shown in Supplemental Fig. 4, the 2\textsuperscript{nd} order harmonic force constants generate the dispersion of GaAs and AlAs well matching the experimental data, which confirms the validity of used parameters. [8, 9].

The 3\textsuperscript{rd} order force constants are obtained through the small displacement method which is prepared and extracted with an auxiliary package, thirdorder.py, in ShengBTE with first principle force calculations in QE. A $4 \times 4 \times 4$ supercell with an interaction range up to the 3\textsuperscript{rd} atomic neighbors is used in the calculation.

In order to calculate the accumulated thermal conductivity of $\kappa_{\text{HSL}}$ as a function of mean free path, it is useful to apply the following change of variable to Supplemental Eq. 3:

$$d\omega = \left(\frac{d\ell}{d\omega}\right)^{-1} d\ell$$

where $\ell = v\tau$ is the phonon mean free path. Supplemental Equation 3 can be
rewritten [22]:

\[
\kappa_{HSL}(L, T) = -\frac{1}{3} \sum_j^L \int_0 C_{\text{SL},j}(T, \omega) v_{\text{SL},j}(\omega) \ell_{\text{SL},j}(\omega, L, T) \left(\frac{d\ell_j}{d\omega_j}\right)^{-1} d\ell_j
\]  

(14)

where the negative sign is included because \(d\ell/d\omega\) is negative as a result of the mean free path decreasing with the increase in frequency. The upper integration limit is \(L\) because the boundary scattering term in our model limits the maximum mean free path to the thickness of the thin film.

Now we analyze the phononic spectral contribution to the thermal conductivity without the effects from the internal interfaces by calculating the mfp distribution, \(\ell_j(\omega, L, T)\) and the thermal conductivity accumulation functions, \(\alpha(\ell, L, T)\) and \(\alpha(\omega, L, T)\) over phonon mfps and frequencies, respectively. The calculation in this case is based on \(\kappa_{HSL}\) and thus does not include contributions from the interfaces. For bulk and thin film SLs of thicknesses 24, 100, and 1,000 nm, Supplemental Fig. 9A shows the mfp \(\ell_j(\omega, L, T) = v_j(\omega)\tau_j(\omega, L, T)\) for the longitudinal and transverse acoustic branches at room temperature where \(v_j\) and \(\tau_j\) are the phonon group velocity and scattering times. The film boundary scattering term limits the maximum mfp in the SL to the thickness \(L\). In other words, phonons with \(\ell > L\) do not exist in the phonon spectrum of the SL. The mfp in a bulk SL shows a strong spectral dependence where phonons of different frequencies have significantly different values of \(\ell_j\). As the film thickness decreases, \(\ell_j\) flattens and a larger portion of phonon frequencies take mfp values closer to the film thickness (i.e., closer to the maximum mfp).

The effect of film thickness on thermal conductivity can be better seen in Supplemental Fig. 9B where we plot \(\alpha(\ell, L, T)\). As the thickness increases, this mean free path-dependent accumulation function spreads over a larger portion of the mfp spectrum and becomes more evenly distributed. To better visualize this, we plot \(\alpha(\ell, L, T)\) for 24 and 100 nm on a linear scale in the inset of Supplemental Fig. 9B. The horizontal and vertical lines in the inset show that based on our model, 50% of thermal conductivity is carried by the upper 28% (17-24 nm) and 55% (45-100 nm).

Supplemental Table 3: Fraction of thermal conductivity carried by phonons with mfp larger than \(L/2\) or frequency lower than than \(\omega_{\text{max}}/2\)

<table>
<thead>
<tr>
<th>Thickness, (L) (nm)</th>
<th>24</th>
<th>100</th>
<th>1,000</th>
<th>bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1 - \alpha_H(\ell, L/2, T)) (%)</td>
<td>82</td>
<td>43</td>
<td>9.4</td>
<td>-</td>
</tr>
<tr>
<td>(\alpha_H(\omega_{\text{max}}/2, L, T)) (%)</td>
<td>48</td>
<td>54</td>
<td>66</td>
<td>76.7</td>
</tr>
</tbody>
</table>
Supplemental Figure 9: (A) Mean free path distribution function in the longitudinal acoustic (LA) and transverse acoustic (TA) branches for a SL sans interfaces plotted versus phonon angular frequency. (B) Thermal conductivity accumulation function, $\alpha(\ell, L, T)$, plotted versus mean free path. (C) Thermal conductivity accumulation function, $\alpha(\omega, L, T)$, plotted versus $\omega$. All plots are at room temperature.

of the phonon spectrum for the 24 and 100 nm films, respectively. This demonstrates how long mfp phonons are more dominant in thinner films. The same can be observed in Supplemental Fig. 9C which plots the phonon frequency-dependent thermal conductivity accumulation. As the thickness decreases, the percentile contribution from low frequency phonons (i.e, long mfp) becomes more substantial. The horizontal and vertical lines show that 50% of thermal conductivity is dictated by the lower 28.7% and 53% of the phonon spectrum in bulk and 24 nm thick samples, respectively.

The analysis presented in Supplemental Fig. 9 clearly explains the ballistic behavior of phonons observed in AlAs-GaAs SLs. In fact, this result can be general-
ized on all thin film structures. As the thickness decreases, the spectral contribution to thermal conductivity becomes more dependent on long mfp (low frequency phonons). Table 3 shows the fraction of thermal conductivity carried by phonons with mfps longer than $L/2$ or with frequencies lower than $\omega_{\text{max}}/2$, where $\omega_{\text{max}}$ is the maximum cutoff frequency. For instance, for $L = 24$ nm, 82% of the thermal conductivity is carried by phonons with mfp between 12 and 24 nm. This percentage decreases to only 9.4% for $L = 1,000$ nm. These results show the strong influence of long mfp phonons on the thermal conductivity of thin films. The increased effect of short mfp phonons for larger thicknesses causes the plateau (leveling off) of the thermal conductivity at higher thicknesses shown in Fig. 1 of the main document. It is also important to note that the thermal conductivity values of films with $L < 200$ nm for the different period thicknesses are closer in value to each other than those among the thicker films. This stems directly from the dominance of long mfp phonons in thinner films that reduces the portion of phonons available for short range boundary scattering. As the thickness increases, short mfp phonons dominate the spectrum and $\kappa_{\text{SL}}$ becomes solely dependent on $d_{\text{SL}}$.

We note that the use of a thin film accumulation function is more direct for comparing to thermal conductivity measurements than the typically used ratio of film to bulk thermal conductivity ($\kappa_{\text{film}}/\kappa_{\text{bulk}}$) accumulation function [22] or the bulk accumulation [23], as it illustrates the relative importance of the different portions of the mfp spectrum in the thin film structure. While $\kappa_{\text{film}}/\kappa_{\text{bulk}}$ can interpret how a thin film thermal conductivity is affected by its dimension as compared to bulk, it does not provide direct insight into the spectral dependence of thermal conductivity in a film of a specific thickness.

References


