Tuning Phonon Transport: From Interfaces to Nanostructures

A wide range of modern technological devices utilize materials structured at the nanoscale to improve performance. The efficiencies of many of these devices depend on their thermal transport properties; whether a high or low conductivity is desirable, control over thermal transport is crucial to the continued development of device performance. Here we review recent experimental, computational, and theoretical studies that have highlighted potential methods for controlling phonon-mediated heat transfer. We discuss those parameters that affect thermal boundary conductance, such as interface morphology and material composition, as well as the emergent effects due to several interfaces in close proximity, as in a multilayered structure or superlattice. Furthermore, we explore future research directions as well as some of the challenges related to improving device thermal performance through the implementation of phonon engineering techniques. [DOI: 10.1115/1.4023584]

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1 Introduction
Thermal performance has become a limiting factor in the progress of many technologies, especially with the proliferation of devices that incorporate nanoscale structures. Microelectronics and energy conversion, industries of major modern relevance, feature several examples of such technologies. Thermal bottlenecks have been a primary impediment to improving microprocessor speeds [1]. The development of viable thermoelectric devices, which could scavenge energy from waste heat, depends partly on the ability to engineer materials with lower thermal conductivity [2]. Quantum cascade lasers, a promising technology for achieving terahertz frequencies in sensing and communications, remain constrained to cryogenic operating temperatures because of electron–phonon interactions [3]. Phase change memory requires simultaneous engineering of thermal and electrical properties to accelerate switching speeds and reduce programming current, potentially leading to memory that is both faster and more energy efficient [4]. These are among the technological problems that have motivated a great amount of research in nanoscale thermal transport over the last few decades. In particular, structures appear in all of these applications that incorporate nano- and microscale features. The thermal limitations facing these applications do not have straightforward solutions, due in large part to relatively limited control of thermal transport compared to electronic transport [5].

Hence, in this paper we survey recent research on phonon transport in layered structures, especially in the context of heat transfer. Models of phonon transport in bulk materials are relatively well developed, but in nanoscale systems, interfaces and boundaries are at least as important as bulk properties to overall transport. This is true of structures in all of the opening examples. Despite decades of research, models of interfacial effects remain much less mature, and are a major impediment to understanding transport in layered structures. A detailed background discussion of phonon transport physics is beyond the scope of this review, and is covered in texts such as the one by Chen [6]. We also refer to the previous review by Cahill et al. [7] for extensive discussion of phononic heat transfer in nanoscale systems to that point, and to the recent review by Pop [1] especially in the context of microelectronics. The effects of interfaces on transport can be broadly categorized by comparing characteristic layer thicknesses \( d \) with the mean free paths \( \lambda \) of phonons that contribute significantly to transport. This distinction can be simplistic because of the broadband nature of phonon transport and the potentially strong variation of \( \lambda \) for different phonon frequencies. However, in the far limit that \( d \gg \lambda \), a layered structure is effectively decoupled into a series of single interfaces. We discuss single interfaces in Sec. 2, with emphasis on the ability to tune their thermal conductance. Many interesting structures also fall in regimes where \( d \sim \lambda \) or \( d < \lambda \). In these cases the analysis of phonon scattering at a single interface is affected by the proximity of nearby interfaces. For the purposes of our discussion, we divide these layered structures into two broad categories, again with attention to strategies for tuning thermal transport. In Sec. 3 we discuss superlattices and multilayers; that is, extended structures with many layers, typically repeating between two materials. In Sec. 4 we discuss polyjunctions, which we define as structures with few layers in which repetition is not an important feature. In each section we also discuss potential future research problems relevant to those structures. Finally, we summarize the review in Sec. 5.

2 Interfaces
Interfaces have an intrinsic resistance to heat flow across them due to phonon scattering caused by abrupt changes in crystallography. In order to facilitate device thermal modeling, the microscopic details of interfacial phonon transport are aggregated into a single macroscopic parameter, the thermal boundary conductance \( h_{BD} \), which is the inverse of the thermal boundary resistance, that relates the temperature discontinuity at the interface to the applied flux:

\[
q = h_{BD} \Delta T
\]  

where \( q \) is the heat flux normal to the interface, and \( \Delta T \) is the temperature discontinuity. Since the observation of \( h_{BD} \) in 1941 by Kapitza [8], researchers have sought a predictive model for \( h_{BD} \). At the most fundamental level, phononic properties depend on the wavevector and phonon transport is described in wavenumber space. However, it is convenient to perform analysis in frequency space, in terms of both ease of calculation and interpretation. For
an ensemble of phonons incident on an interface, the transport across is described within the Landauer formalism by [6]

\[ h_{BD} = \frac{1}{2} \int_0^{\infty} \left[ \sum_j \int_0^{\omega_j} \sigma_{\text{phonon}}(\omega) \sigma_{\text{transmission}}(\omega-\omega_j) \frac{\partial f(\omega,T)}{\partial T} d\omega \right] \mu d\mu \tag{2} \]

where \( j \) denotes a phonon branch, \( \omega_j \) is the cut off frequency for branch \( j \), \( h \) is the reduced Planck constant, \( \omega \) is the angular phonon frequency, \( v_j \) is the phonon group velocity, \( \sigma_{\text{transmission}} \) is the transmission probability from side 1 to side 2, \( \mu \) is the cosine of the incidence angle, \( D_j \) is the spectral phonon density of states of branch \( j \), and \( f \) is the Bose–Einstein distribution. This formulation is derived from the wavevector description under the assumptions of small temperature differential across the interface and isotropic dispersion. The main difficulty in carrying out this calculation is in the prediction of the transmission probability, which differentiates the various approaches to modeling \( h_{BD} \).

Early attempts at modeling the thermal boundary conductance used an analogy to classical wave theory and acoustics. The resulting acoustic mismatch model (AMM) calculates the transmissivity based on the acoustic impedances of the constituent materials, giving in the simplest case of a phonon with transverse polarization perpendicular to the plane of incidence [6,9]:

\[ \sigma_{\text{transmission}}(\omega) = 1 - \frac{Z_1 \mu - Z_2 \cos \theta}{Z_1 \mu + Z_2 \cos \theta} \tag{3} \]

where \( Z \) is the acoustic impedance of the material given by the product of Brillouin zone center group velocity and density \( Z = v \rho \). 

The relative vibrational properties of the materials that constitute the interface

Both the AMM and DMM capture the aspects most important to interfacial thermal transport: the mismatch in material vibrational properties and the phonon population incident on the interface. The AMM takes the acoustic impedance as the critical vibrational property, while the DMM considers the product of group velocity and the density of states. The phonon population is dictated by the temperature, which enters the model through the Bose–Einstein distribution and the density of states. Nevertheless, the treatment thus far of \( h_{BD} \) has neglected the characteristics of the interface itself. Several modifications have been made to the DMM in recent years in order to more accurately calculate the \( h_{BD} \) of interfaces where the structure is known to diverge from the ideal interface. The use of Debye dispersion has been replaced by isotropic dispersion with [12] and without [13] optical branch contributions or full dispersion [14], inelastic scattering has been considered in addition to elastic scattering [15–17], and the effects of interface disorder [18–22] have all been recently considered.

The myriad issues that have been addressed in order to make the DMM conform to experimental observations illustrate the complexity of the problem of interface conductance while providing an overview of the factors that determine it. The two factors that have the greatest influence on \( h_{BD} \) are the vibrational mismatch of the materials that comprise the interface and the temperature of the system. The former is included explicitly in both the AMM and DMM, and the temperature dependence manifests itself not only in the change in the phonon population, but also through a change to the phonon dispersion and increased inelastic scattering at the interface [17]. The interface bond strength and system pressure also affect \( h_{BD} \) by modifying the mode dependent transmissivity of different phonons. The mismatch, temperature, interface bond strength, and pressure are all parameters which, although they influence \( h_{BD} \), are characterized by limited controllability in actual device applications. However, modifications to the local interface structure offer the ability to tune \( h_{BD} \) independently of bulk material and environmental conditions. Parameters that belong to this category include the interface roughness, interdiffusion, and defect density. The ranges over which \( h_{BD} \) have been experimentally tuned using these methods are collated in Fig. 1.

### 2.1 Interface Vibration Mismatch

The relative vibrational properties of the materials that constitute the interface

**Fig. 1** Tuning of \( h_{BD} \) achieved in experiments by roughness (Sec. 2.5), interdiffusion (Sec. 2.6), and defects (Sec. 2.7) at room temperature. In actual systems, each interface condition will be accompanied, to some extent, by the others. Thorough characterization of the interface is essential in experiments seeking to understand the effects of interface conditions on \( h_{BD} \).
figure prominently in both the AMM and DMM. In general, materials with similar vibrational properties will have a higher transmissivity, while the converse is true for mismatched materials. Using the Debye temperature as a proxy for the vibrational properties of materials, Stoner and Maris [11] confirmed that $h_{BD}$ tends to decrease with an increase in the mismatch. At larger Debye temperatures, mismatches, $h_{BD}$ exceed the maximum value permitted by elastic scattering, meaning that inelastic scattering channels have a significant effect. This result is supported by Stevens et al. [23] and Lyeeo and Cahill [24], who found that $h_{BD}$ of highly mismatched interfaces exceeds that predicted by the DMM and phonon radiation limit, respectively.

Molecular dynamics simulation offers the ability to isolate the effects of changes to the vibrational mismatch between materials. Simulations have been conducted that vary the vibrational spectrum of one side of the interface, often by altering the mass, but also by adjusting the interatomic potential. Twu and Ho [25] used the potential well widths of the Lennard-Jones and Morse potential as a proxy for the mismatch and found an approximately exponentially decrease in $h_{BD}$ with increased mismatch. Using the ratio of Debye temperatures, Stevens et al. [26] found a decrease in $h_{BD}$ with greater mismatch. Hu et al. [27] adjusted the bond strength of silicon in a Si/polysilicon system. They found a power law decrease in $h_{BD}$ with an increase in the stiffness of the silicon. Landry and McGaughey [28] modified the mass of silicon in a Si/heavy-Si system and found that $h_{BD}$ decreased with increased mismatch. Lyver and Blaisten-Barojas [29] confirmed the trend of decreased $h_{BD}$ with mismatch. Wang and Liang [30] examined a Al/Heavy-Ar interface and found a linear increase in thermal boundary resistance with mismatch. The trend was also confirmed by Ju et al. [31]; they show that above a mass ratio of 3, the boundary conductance as computed in MD is less than the DMM and AMM predict, whereas it is higher below 3. Finally, Shen et al. [32] found a linear trend of conductance with mass ratio.

The issue of vibrational mismatch is further complicated by the fact that the density of states is altered from that of the bulk near the interface [29,31,33–35]. Specifically, high frequency modes appear and the lower frequency modes are softened in the softer material [29,33]. The effect of the interface on the local density of states was not observed in the work of Ju et al. [31], although, according to the authors, this could be because the small system sizes studied diminished the distinction between interface and bulk atoms. The alteration of the density of states in the vicinity of the interface and the effect of this on $h_{BD}$ is difficult to ascertain. Experimental observation of this effect, and incorporation of it into future models of $h_{BD}$, may improve the ability to predict $h_{BD}$. It is likely that the local density of states will affect incoming phonons differently based on their wavelength and/or mean free path in comparison to the scale of the affected interfacial region.

2.2 Interface Temperature. In the elastic formulation of the DMM, $h_{BD}$ has temperature dependence only through the Bose–Einstein distribution. Consequently, the lower Debye temperature among the interface materials is a critical temperature when considering transport. Below this temperature, $h_{BD}$ increases with temperature as more modes become available to participate in the transport. In the low temperature limit, $h_{BD}$ grows as $T^3$ according to the Debye model of heat capacity [6]. Above the lower of the two Debye temperatures, Eq. (2) predicts a constant $h_{BD}$ since there are no new modes available for elastic scattering, either on one side of the interface or the other. However, experimental studies of the temperature trend by Lyeeo and Cahill [24] and Hopkins et al. [36,37] show a clear increase in $h_{BD}$ with temperature, in disagreement with theories discussed so far. This disagreement is attributed to the onset of inelastic phonon scattering, whereby multiple phonons can combine and/or split when scattering at the interface, relaxing the restrictions imposed by conservation of energy.

Once the system temperature exceeds the larger Debye temperature, the system has reached the classical regime where all phonon modes are excited. These conditions correspond to thermal modeling of materials with classical molecular dynamics simulation, where all vibrational modes are excited at all temperatures. Molecular dynamics simulations by Stevens et al. [26], Hu et al. [27], Luo and Lloyd [38,39], and Duda et al. [41] show a linear increase in $h_{BD}$ with temperature. Other simulations also support a monotonically increasing thermal boundary conductance with temperature [28,30,31,40]. This result supports the experimental findings. Furthermore, the same mechanism proposed to explain experimental results is also present in the simulations; anharmonicity of the interatomic potential permits inelastic scattering.

Inelastic phonon scattering at the interface has been treated theoretically by Hopkins et al. [16,17] and Duda et al. [41] using two different mechanisms. In the work of Hopkins et al. [16,17], the two-phonon elastic transmission is calculated normally and then the principle of detailed balance is applied to the remaining phonons that would have been reflected had they been unable to participate in inelastic processes. This is repeated for up to N-phonon processes, resulting in better agreement with experimental data. In the second mechanism, Duda et al. [41] proposed that the high temperature linear trend is actually due to phonon-phonon scattering. In their model, it is argued that low wavenumber phonons can ignore the interface and undergo phonon-phonon scattering after traversing the interface. This process is reminiscent of evanescent modes penetrating into a material [6]. The temperature dependence arises from models of thermal conductivity where the phonon-phonon scattering rate is proportional to the temperature at high temperatures [42–44].

2.3 Interface Bonding. The fact that bulk material properties are used in the formulation of the AMM and DMM implies that they model an ideally bonded interface, that is, one with an infinite spring constant [45]. In actual materials, the bond strength at the interface is finite and its value affects $h_{BD}$. Young and Maris [46] used a lattice dynamical model to investigate the effects of the interface bonding in a spring-mass system. They found that the bonding had little effect for the range of strengths between those of the bulk materials. Above this range, the effect of bond strength was slight, and for bonds at the interface weaker than those in the bulk, $h_{BD}$ scaled quadratically with the bond strength. The quadratic trend for weak interfaces has been confirmed in subsequent, acoustical modeling [45,47]. In these models, two different parameters are used to characterize the interface bonding condition: the bond energy and the spring constant $k$, and both show the same trend.

To elucidate the relationship between material interfaces, bond energy, and spring constant, we consider the Lennard-Jones potential. Although this potential is only well suited for the modeling of van der Waals interactions, it captures the basic underlying principles common to all types of bonding. The form of the potential is

$$ u = 4\varepsilon \left[ \frac{\sigma^6}{r^6} - \frac{\sigma^12}{r^12} \right] $$

where $u$ is the energy of the pair interaction, $\varepsilon$ gives the depth of the energy well, $\sigma$ is a length parameter determining equilibrium separation distance, and $r$ is the separation distance between two atoms. Taking a Taylor expansion of the potential about the equilibrium separation distance, it can be seen that $k \propto \varepsilon$, which explains why $h_{BD}$ has the same trend with respect to both the spring constant and bond strength in the models. Most real interfaces will be in the regime of growing $h_{BD}$ with stronger bonding because of considerations of interface thermodynamic stability. One condition for a stable interface is that the energy associated with those bonds must be higher (less negative) than the bonds in the bulk [48], otherwise the materials will mix in order to obtain a
lower system energy. This places the typical interface in the weakly bonded regime described by Young and Maris [46].

Molecular dynamics simulations have confirmed the general relationship between bond strength and $h_{BD}$, although simulations have shown a roughly linear trend for Si/amorphous-polyethylene [27], carbon nanotube/SiO$_2$ [50], Si/Ge [51], Cu/SiO$_2$ [52], and Lennard-Jones solid-solid [32] and solid-liquid [53] systems. The reason for the difference between the quadratic trend predicted by theories concerned with interfacial bonding [45,46,47] and the observed trend in simulations is unclear.

Experimentally, Losego et al. [54] harnessed the effect of bonding to tune $h_{BD}$ at a Au/self-assembled-monolayer (SAM) junction by varying the functional group termination of the SAM. Using this method, the authors were able to tune $h_{BD}$ over the range of about 35 to 65 MW m$^{-2}$K$^{-1}$. Also using a molecular layer approach, O’Brien et al. [52] tuned the overall $h_{BD}$ of a Cu/molecule/SiO$_2$ interface over the range of 260 to 430 MW m$^{-2}$K$^{-1}$, which also represented a dramatic increase over the baseline Cu/SiO$_2$ $h_{BD}$ of 90 MW m$^{-2}$K$^{-1}$. Collins et al. [55] tuned $h_{BD}$ between aluminum and single crystalline diamond using hydrogen and oxygen surface treatments of the diamond, achieving tuning in the range of 19 to 91 MW m$^{-2}$K$^{-1}$. The oxygen terminated diamond surface offered stronger bonding with the aluminum than the hydrogen, leading to higher values of $h_{BD}$. Using a similar method, Hopkins et al. [56] functionalized single layer graphene with oxygen or hydrogen to tune the $h_{BD}$ of an Al/graphene/SiO$_2$ interface in the range of 23 to 42 MW m$^{-2}$K$^{-1}$. The use of SAMs and adatoms to improve $h_{BD}$ parallels current research into inorganic materials for the same purpose (see Sec. 4.1). As this approach becomes more common, these results indicate that chemical functionalization will be an effective method for tuning $h_{BD}$.

2.4 Interface Pressure. Related to the effect of bond strength is the effect of applied pressure. The application of pressure alters the equilibrium separation distance of atoms, disrupting covalent bonding atoms with weaker bonding. This changes both the vibrational properties of the materials comprising the interface and the force interaction between interfacial atoms. By changing the vibrational properties of the bulk materials, the mismatch is changed, altering $h_{BD}$ as discussed in Sec. 2.1. Simulations by Shen et al. [32] and Liu et al. [57], and experiments by Hsieh et al. [58] indicate that the interfacial thermal conductance increases linearly with the applied pressure for weakly bonded interfaces. Referring to Eq. (5), by expanding the pair potential in a Taylor series, it can be shown that a compressive pressure increases both the harmonic and higher order force constants and vice versa for a tensile pressure. Thus, the applied pressure tunes $h_{BD}$ primarily through the change to the interface spring constant, but also through a change in inelastic scattering.

2.5 Interface Roughness. We now turn to those methods that offer the ability to tune $h_{BD}$ independently of the interface materials and environmental conditions. A roughened interface is one for which the interface is nonplanar, yet still exhibits a sharp change in material composition. There are a couple of parameters to quantify the roughness of an interface. The first is the root mean square (rms) height of the interface features. The second is the correlation length, which is a measure of the lateral distance between similar features of the interface topology [59]. Both parameters can be derived from measurements of the surface profile before deposition of the second material, using a microscopy technique such as atomic force or scanning tunneling microscopy. Theory predicts that roughness will increase $h_{BD}$ due to an increase in diffuse scattering. Kechrakos [60,61] predicted an increase in $h_{BD}$ across all temperatures for an interface with roughness on the order of a monolayer and an enhancement of about 2 to 3 times for a roughened interface above the Debye temperature for moderately mismatched materials. Fagas et al. [62] also theoretically treated interface roughness in the limit of a single monolayer. Varying the correlation length of mass impurities at the monolayer/thick film interface, they found that the phonon transmissivity has a strong dependence on phonon frequency and the roughness correlation length. Both rms roughness and correlation length can be incorporated into a single Fourier spectrum description. Taking this approach with a Green’s function analysis, Zhao and Freund [59] showed that the specularity of the interface depended primarily on the interface rms roughness and not the correlation length. Even so, in the limit of a small interface temperature discontinuity, the authors found that $h_{BD}$ was relatively insensitive to both the rms roughness and correlation length, at least over the range of values investigated. A study by Sun and Pipe [63] used a modeling approach that treats roughness as a perturbation to a perfectly flat interface. Their results largely corroborate those of Zhao and Freund [59], in that the correlation length of the roughness does not have a strong effect. Their work covers many of the aspects of specular and diffuse scattering. Roughness acts to decrease specular transmission and reflection for each polarization across all incidence angles. In comparison to the DMM, they found that transmitted (and reflected) modes are preferentially concentrated near the incident phonon wavenumber. Only the amplitude of this distribution is affected by the mismatch in material vibrational properties. Finally, the authors demonstrate the presence of evanescent modes under certain conditions of phonon incidence.

In contrast to the theoretical results that predicted an increase in $h_{BD}$ with roughness, experimental observations have indicated a strong, decreasing trend. Decreasing $h_{BD}$ with roughness has been observed experimentally for an Al/Si interface [20,64], Al/GaAs interface [21], and an Al/Si interface with quantum dot roughening [22]. One explanation for the opposite trend is that, experimentally, a roughened interface is typically accompanied by various crystallographic defects, obfuscating the direct relationship between the roughness and $h_{BD}$. Nevertheless, the authors were able to use roughness to tune $h_{BD}$ in the range of about 90 to 193 MW m$^{-2}$K$^{-1}$ for the Al/Si interface [64], 15 to 29 MW m$^{-2}$K$^{-1}$ for the Al/GaAs interface [21], and 105 to 170 MW m$^{-2}$K$^{-1}$ for the quantum dot interface [22]. In these examples, interface roughness was achieved through wet chemical etching, deposition conditions, and quantum dot growth conditions, respectively.

2.6 Interface Interdiffusion. Interdiffusion of the two materials comprising the interface is another factor that influences $h_{BD}$. Whereas interface topology is the defining parameter of roughness, the species concentration distribution across the interface is the key parameter for interdiffusion. Transport across diffuse interfaces was treated theoretically by Beechem et al. [18], where the disordered region was treated as its own material with weighted properties of the elements involved. Their model predicts a minimum in $h_{BD}$ for intermediate mixing of materials in the alloyed interfacial region and shows reasonable agreement with experimental results.

Simulations investigating the effects of interdiffusion display varied results. Simulations by Liang and Sun [65], Stevens et al. [26], and English et al. [35] of Ar-heavy-Ar systems show an increase in $h_{BD}$ with moderate interdiffusion. This is in contrast to other simulations by Twu and Ho [25], Li and Yang [51], and Choi et al. [66] that found a decrease in $h_{BD}$ for an Ar/Ar system, a Si/Ge system, and an Al/Si system, respectively. A notable difference between these sets of simulations is that the materials were lattice matched when $h_{BD}$ increased and not lattice matched when it decreased. The relationship between interdiffusion and $h_{BD}$ may also be sensitive to the particular functional form of the
concentration profile, making comparisons between different simulations (and experiments) tenuous [35]. Experimental results of a Cr/Si interface by Hopkins et al. [19,67] show that interdiffusion can be used to tune $h_{BD}$. The studies showed that the largest conductance values were obtained when the concentration gradient of the species transitioning across the interface was small. The concentration gradient was controlled through the deposition conditions. The thickness of the mixing region also played a role, but perhaps only insofar as a thicker mixing region enables a smoother transition from one material to the other. Using interdiffusion, the authors tuned $h_{BD}$ in the range of about 113 to 178 MW m$^{-2}$ K$^{-1}$. The complex role of the species concentration distribution is supported by the simulation study by English et al. [35], who show that the thermal boundary conductance is a nonmonotonic function of the degree of interdiffusion.

2.7 Interface Defects. Just as with bulk conduction, the presence of defects at the interface provides an additional mechanism by which phonons can scatter, affecting $h_{BD}$. All nonidealties of an interface that do not correspond to roughness or interdiffusion, as discussed in previous sections, will be treated under the same broad category of defects in this section. Defects arising from lattice mismatch and impurity atoms are two examples. The distinction among the various interface nonidealities is complicated by the fact that both roughness and interdiffusion invariably introduce other crystallographic defects, and that models developed for nonideal interfaces do not always attempt to distinguish between the different aspects, as covered here.

Models by Kozorezov et al. [68] and Prasher and Phelan [69], while developed for a generic, nonideal interface, will be applied here as meaning an interface with defects. The model by Kozorezov et al. [68] treats a defective region in the vicinity of the interface as its own material and determines the relative contributions of specular and diffuse scattering. The model by Prasher and Phelan [69] predicts $h_{BD}$, while considering phonon scattering in the vicinity of the interface; i.e., the phonons that interact with the interface may not have a bulk-like distribution. Simulations by Li and Yang [51] display a reduction in $h_{BD}$ with vacancy size and concentration.

Experimental results also indicate a decrease in $h_{BD}$ with defect density. In one study, Hopkins et al. [21] tuned the strain dislocation defect density of a GaSb/GaAs interface; modifying the width of the defected region leads to tuning of $h_{BD}$ from 12 to 21 MW m$^{-2}$ K$^{-1}$. In another study, Hopkins et al. [70] used proton ion implantation to add defects to Al/Si and Al/Al$_2$O$_3$ interfaces which led to the ability to tune $h_{BD}$ in the range of 25 to 200 MW m$^{-2}$ K$^{-1}$ and 12 to 310 MW m$^{-2}$ K$^{-1}$, respectively, although some mechanisms beyond the defects may also have contributed [71]. Norris et al. [72] used various surface cleaning methods to alter the interface structure and chemical impurities of a Au/highly-ordered-pyrolytic-graphite system, leading to the ability to tune $h_{BD}$ in the range of 7 to 31 MW m$^{-2}$ K$^{-1}$.

Although it does not offer the same control and range of tunability, the deposition method and parameters offer an additional route to tuning $h_{BD}$. In a study by Kato and Hatta [73], Au was deposited on SiO$_2$ using evaporation and sputtering with different deposition rates. The $h_{BD}$ of the evaporation deposited interface was about 122 MW m$^{-2}$ K$^{-1}$, and for the sputtered interface it was about 31 MW m$^{-2}$ K$^{-1}$. In a similar study, Monachon et al. [74] also examined the effect of evaporation and sputtering on $h_{BD}$. The surface quality before deposition affected the relationship between the evaporated and sputtered values. They measured an evaporated conductance of 43 MW m$^{-2}$ K$^{-1}$ and a sputtered value of 171 MW m$^{-2}$ K$^{-1}$ on the untreated interface. On an interface cleaned by reactive-ion etching, the values were 241 and 186 MW m$^{-2}$ K$^{-1}$ for the evaporated and sputtered interface, respectively.

2.8 Interface Research Outlook. In this section we have discussed investigations of interfacial thermal transport by theoretical, simulated, and experimental means, with attention to how interface structure can be modified in order to tune phonon transport. Significant progress has been made in the understanding and engineering of interfacial thermal transport in the past decade. Of particular note are the strides made in the realms of modeling and simulation where increased computing power has enabled virtual studies of great complexity and sophistication, complementing the experimental investigations. Yet, we now turn our attention toward specific aspects of research where we believe coordinated effort would greatly profit the field of nanoscale thermal transport.

First, we note that our discussion has been restricted to interfacial transport involving phonons only. Experimental evidence has suggested that metal/insulator interfaces can often be treated as phonon dominated, neglecting the direct energy transfer between electrons in the metal and phonons in the nonmetal [11,24]. However, some theoretical [75–77] and experimental [78,79] studies have shown that the transport through this channel might be significant, and attempts to tune interfacial conductance may need to consider this mechanism in some systems, such as the Au/Si interface. Although a detailed discussion of electron-phonon interactions is beyond the scope of this work, we highlight this as an important question for future research, given the ubiquity of metal/nonmetal interfaces in device applications, as well as their importance in thermal metrology at the nanoscale.

Despite the numerous modifications to the DMM that have improved its correlation with experimental data, many interfaces are not completely diffusive, lying somewhere between specular and diffuse on the spectrum of interface conditions [63,80]. Recent simulated results that demonstrate the modification to the density of states near the interface, compared to the bulk, imply that, from the perspective of the phonons, the interface is a much larger construct than a mere infinitesimal plane [29,31,33–35], extending at least as far as the strain relaxation distance. As such, we encourage pursuit of a model that treats phonon scattering in the bulk, near an interface, and at the interface using the same general framework. In this direction, one wonders if the scattering rates can be inferred from the variation in the occupied density of states near an interface.

Simulations have demonstrated their worth with respect to isolating parameters that influence thermal boundary conductance, measuring system properties and dynamics with atomic resolution, and determining trends. However, there are, as of yet, very few studies that attempt to recreate experimental conditions where two or more mechanisms influence thermal boundary conductance. The increasing accessibility of computing power should allow such inquiries into the atomic-scale explanations of transport behaviors that are experimentally observed.

Finally, if interfacial structure is to be harnessed in order to tune thermal transport in actual devices, a highly detailed understanding of the interfacial structures that correspond to measured values of thermal boundary conductance is required. We encourage experimentalists to characterize the interfacial structures that they study to the fullest extent possible. This will facilitate the development of models and help to isolate the contributions of different interface mechanisms, better enable simulations to corroborate results, and, ultimately, hasten the technological implementation of sophisticated, engineered interfaces.

3 Multilayers

Multilayers, and the special case of superlattices, are structures composed of many layers in a periodic sequence. They have inspired much research related to low phononic thermal conductivity $k$, which arises from suppressed phonon transport. These structures are relevant in a variety of applications; in some systems, the low $k$ is a desirable feature (e.g., thermoelectrics, thermal barriers), while in others it might be a side effect of engineering other properties (e.g., optoelectronics such as quantum cascade lasers). In either case, the ability to engineer thermal properties requires an understanding of underlying phonon

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behavior. Besides their relevance in these applications, superlattices in themselves also provide a rich context for studying the fundamental science of phonon transport. To date, research has focused on structures alternating between two materials (i.e., two layers per period, ABAB). Regarding terminology, we will use the term “multilayer” to refer to these structures in general. We will follow the convention of reserving the term “superlattice” for the special cases when the layers are themselves single crystalline, in which case the combined symmetries of the crystal lattice and the superlattice are potentially important. However, both terms are used with varying scope in the literature, and the distinction is not always clear; the transport in these structures is complex and defies easy categorization.

3.1 Models for Multilayer Transport. The comparison between the thickness of layers in a multilayer (or, similarly, the period length \( L \)) and the dominant phonon mean free path \( \lambda \) often serves as a rough proxy for the distinction between diffusive and ballistic phonon transport. Phonons that dominate thermal transport in common crystalline materials are thought to have \( \lambda \) spanning several orders of magnitude, 10 nm to 10 \( \mu \)m \([7,81,82]\). When layer thicknesses are much greater than \( \lambda \), many phonon-phonon scattering events occur in the material between interfaces. Phonon transport is diffusive, and heat transfer is modeled well by a conventional thermal resistance network. Section 2 discusses the various nanoscale effects involved in analyzing interfacial resistances. Otherwise, we will not discuss this case here.

We focus on the regime where distances between interfaces are on the scale of \( \lambda \) and smaller. This corresponds to a transition to ballistic transport, in which interface scattering dominates and little phonon-phonon scattering occurs in the layers. The resistance network model for heat transfer breaks down. Within this regime, phonon transport may also differ in exhibiting particlelike (incoherent) and/or wavelike (coherent) behavior, as distinguished by the presence of interference among phonons. The Boltzmann transport equation (BTE) serves as the typical basis for incoherent models \([83–86]\). The dominant mechanisms that suppress thermal conductivity are interface and defect scattering, which are assumed to be sufficiently diffusive to destroy coherence. In the other limit, coherent transport models are typically based on harmonic lattice dynamics (LD) to describe wavelike propagation of energy through the atomic lattice \([87–92]\). This presumes that interface scattering is specular and preserves the phase of scattered phonons. In a crystalline superlattice, the phonon dispersion relation reflects the extended periodicity \( L > \alpha \) in the cross-plane direction (lattice parameter \( \alpha \)). In reciprocal space, this shrinks the edge of the first Brillouin zone compared to the bulk, and the phonon dispersion relation is folded inside. This has two important effects: reduced group velocities and the emergence of phononic band gaps. A smaller Brillouin zone would also mean different period lengths. Yu et al. \([108]\) used the same method to gather temperature-dependent data. Thermal measurements of multilayers accelerated with the development of the 3o technique \([109–119]\) and thermorelectance techniques \([120–123]\), which have been used to measure superlattice conductivity \( k \) primarily in the cross-plane direction. In the context of thermal properties, we will emphasize research on cross-plane transport since it has shown greater potential for thermal engineering.

Some important trends in experimental data, especially \( k \), motivate the discussion in the following subsections. The dependence of \( k \) on temperature (Sec. 3.3) has proven most straightforward to interpret across reports. Weak temperature dependence across material systems implies that interface and defect scattering are the dominant suppression mechanisms in most systems, even with some reports showing potential coherent effects. The dependence of \( k \) on period length (Sec. 3.4) has been a more complex subject, and overall trends in the literature are more difficult to discern. Reported trends appear strongly dependent on material systems. This suggests a large role for interfacial quality and defects, which we discuss in Sec. 3.5. The combined insights from this stage for some recent examples of multilayer structures with deliberate thermal design, which we discuss in Sec. 3.6 along with possible avenues for future investigation.

3.2 Experimental Measurements of Multilayers. The aforementioned models provide predictions for different limits of phonon behavior—for example, how coherent and incoherent behavior might make different contributions to the thermal conductivity as a function of period length \( k(L) \). These predicted trends are templates for experimental validation; thus (ideally) enabling researchers to deduce the dominant mechanisms in real multilayers. This dates back to the experiments of Narayanamurti et al. \([103]\), in which the generation and transmission of mono-chromatic phonons exhibited a clear stop band in GaAs/AlGaAs superlattices, signifying coherent transport. Subsequent experiments have reinforced the observation of coherence in various superlattices of III-V materials \([104–106]\). However, in the context of phononic heat transfer, the investigated phonon frequencies are low—on the order of hundreds of GHz. Although these experiments provide clear evidence of coherence at low frequencies (long wavelengths), defects and interfacial features affect shorter-wavelength phonons more strongly, potentially disrupting coherence. Hence, the significance of coherence in aggregate, broadband thermal transport is less clear, and has been inferred only indirectly from thermal measurements.

Measurements of thermal properties in superlattices date back to Yao \([107]\), who used ac calorimetry to measure the in-plane diffusivity and conductivity of AlAs/GaAs superlattices with different period lengths. Yu et al. \([108]\) used the same method to gather temperature-dependent data. Thermal measurements of multilayers accelerated with the development of the 3o technique \([109–119]\) and thermorelectance techniques \([120–123]\), which have been used to measure superlattice conductivity \( k \) primarily in the cross-plane direction. In the context of thermal properties, we will emphasize research on cross-plane transport since it has shown greater potential for thermal engineering.

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3.3 Temperature in Multilayers. Temperature is not typically a free design parameter in device applications, so we discuss it more for insight into underlying transport than as a practical means for controlling conductivity. Among the discussed mechanisms that suppress phonon transport, only umklapp scattering is strongly temperature dependent. This creates the \( T^{-1} \) conductivity trend in bulk crystals at high temperatures, where phonon-phonon scattering dominates. However, for multilayers in the ballistic regime, we assume that this is much less important than interface and defect scattering, which are temperature independent, at least under the basic assumption of elastic phonon scattering. Therefore, the cross-plane conductivity in multilayers is expected only to increase with low temperatures due to quantum mechanical phonon population effects; at higher temperatures, \( k \) should only be weakly temperature dependent.

The possible exception arises if coherent effects are significant, giving rise to mini-umklapp scattering as a significant mechanism. The early theoretical report by Ren and Dow \([93]\) analyzed this
shows no decrease in the conductivity of skutterudite IrSb in disrupting coherence. The report by Song et al. [111] showed no sign of decreasing k with T. In these cases, the lattice mismatch between Si and Ge appeared to play a large role in disrupting coherence. The report by Song et al. [111] also showed no decrease in the conductivity of skutterudite IrSb/CoSb superlattices. The dominant explanation for these mixed reports of coherence has been the disruptive effect of scattering at nonideal interfaces, as expected by Ren and Dow [93].

Experimental measurements of cross-plane conductivity, compiled in Fig. 2, have been generally consistent with theoretical expectations. In structures where no coherent transport is expected, k shows no decrease with T since neither umklapp nor mini-umklapp processes should be important. Such trends are observed in the layered Si/Ge0.3 and Si0.6Ge0.4/Ge0.24 structures studied by Huxtable et al. [115], in which alloy scattering should preclude coherence in all but the lowest-frequency phonons. The same pattern is seen in the data reported by Costescu et al. [122] for W and amorphous Al2O3.

Among superlattices grown epitaxially, evidence for the significance of coherent effects is mixed. As seen in Fig. 2, some decrease in k with T is seen in the data from Capinski et al. for GaAs/AlAs [120], from Borca-Tasciuc et al. for InAs/AlSb [114], and from Cahill et al. for PbTe/PbSe [113]. However, the Si/Ge structures studied by Lee et al. [109] and Borca-Tasciuc et al. [112] showed no sign of decreasing k with T. In these cases, the lattice mismatch between Si and Ge appeared to play a large role in disrupting coherence. The report by Song et al. [111] also showed no decrease in the conductivity of skutterudite IrSb/CoSb superlattices. The dominant explanation for these mixed reports of coherence has been the disruptive effect of scattering at nonideal interfaces, as expected by Ren and Dow [93].

3.4 Period Length in Multilayers. Unlike temperature, the period length L of a structure can be a design choice for controlling thermal conductivity. The effect of L has also been a rich topic for fundamental insight, revealing information about the mean free paths λ of dominant phonons and the transition between particle- and wavelike transport. Equivalently, results have often been reported in terms of interfacial density. We compile selected experimental results in Fig. 3, which shows that trends with L have been much more difficult to interpret than trends with T. In the limit of thick layers, bulk resistances dominate interfacial resistances, and k should be independent of L (i.e., independent of the interface density). As L decreases, a transition toward the ballistic regime corresponds with increased significance of interfacial resistances, and k should decrease with shrinking L. Several early experiments reported this trend down to the shortest period lengths, corresponding to the persistence of particlelike phonon transport [109,115,120,121]. Among these, the trend observed by Capinski et al. [120] does not reflect the coherence suggested by the temperature dependence in the same report, which highlights the complexity of the research problem. More recently, Koh et al. [123] showed a persistence of particlelike transport in AlN/GaN superlattices, dominated by strongly wavelength-dependent interface scattering. This behavior corroborates theoretical predictions of L dependence using the BTE [83–85].

Other experimental reports, however, have suggested a transition to wavelike transport at very short L, as signified by a nonmonotonic trend that gives a minimum in k at short L. Simkin and Mahan [89] predicted this trend theoretically for coherent systems, showing that k should exhibit a minimum around L ∼ λ, marking a transition between particlelike transport for thicker L and wavelike transport for shorter L. This was the proposed
explanation for early measurements of conductivity by Venkata-
subramanian in Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattices [110] and by Chakra-
borthy et al. in Si/Ge [116], as motivated by thermoelectrics. In support of those results, Wang et al. [124] measured sound speeds in Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattices that were 10% lower than predicted from impedance alone, suggesting a lowered group velocity associated with coherence. L dependence has also indicated coherent transport in some more recent conductivity measurements, as reported by Zhang et al. for InGaAs/InGaAsP [117] and by Tong et al. for Ge$_2$Te$_3$/Sb$_2$Te$_3$ [119].

These compiled results show that the identification of dominant mechanisms in superlattice and multilayer transport is a complex problem. At this point, it appears plausible that phonon coherence can have a significant effect on thermal transport, but only in certain systems. Superlattices of III-V materials, for example, appear to be better candidates for significant coherent transport than group IV superlattices. However, the apparent importance of coherent effects has varied even among reports for the same material system; for example, Refs. [109,112,116] for Si/Ge superlattices and Refs. [110,121] for Bi$_2$Te$_3$/Sb$_2$Te$_3$. This implies the intuitive result that the importance of different suppression mechanisms is very sensitive to the particular growth quality of each structure.

As a design parameter for controlling thermal conductivity, the period length is important when interfacial resistances are important (compared with bulk resistances from alloy or bulk defect scattering; for example). In the reports with greatest sensitivity to L, the attainable conductivities range across a factor of 3 or 4 near room temperature. This is the case for the reports by Capinski et al. (about 4 to 14 W m$^{-1}$K$^{-1}$) [120], by Venkata-Subramanian (0.2 to 0.6 W m$^{-1}$K$^{-1}$) [110], by Costescu et al. (0.5 to 1.5 W m$^{-1}$K$^{-1}$) [122], and by Zhang et al. (2 to 6.6 W m$^{-1}$K$^{-1}$) [117].

3.5 Nonideal Interfaces in Multilayers. Nonideal interfaces have been the primary explanation for the difficulty in observing coherent transport in superlattices. In a set of molecular dynamics simulations, Daly et al. [95] demonstrated a clear minimum thermal conductivity as a function of period length, as long as the interfaces were perfect. Interfaces with random, single-atom roughness—confined to only one monolayer at each interface—caused the minimum to disappear, indicating that the slight disorder had disrupted coherent phonon transport. However, a simplistic model was used for GaAs/AlAs, in which a single “average” atom represented each two-atom primitive cell. More recently, lattice dynamics calculations by Ren et al. [90] and MD simulations by Landry and McGaughy [99] demonstrated the same effect in diamond-structure Si/Ge superlattices, in which a similarly small extent of interfacial mixing destroyed coherent effects.

These predictions suggest that coherent effects may not be an important suppression mechanism in experimental systems with even single-monolayer roughness or interdiffusion. However, one significant shortcoming of simulations to date is that their in-plane dimensions have been limited by computational resources to tens of angstroms (i.e., the periodicity enforced in those dimensions). This constrains the correlation length of simulated roughness, as described in Sec. 2.5 for single interfaces. In contrast, monolayer steps at a GaAs/AlGaAs interface grown by molecular beam epitaxy (MBE) may be separated in-plane by hundreds of angstroms, with broad, atomically smooth “islands” in between [125]. Experimentally, Duquesne [118] used growth temperature to explicitly vary the cross-plane extent of interfacial roughness d$_0$ in GaAs/AlAs superlattices and measured the effect on thermal conductivity by 30%. Indeed, the data showed no discernible difference between the sample with “perfect” interfaces (d$_0$ = 0 nm) and the sample with one-monolayer steps about the interfaces (d$_0$ = 0.15 nm), in apparent contrast with predictions. Broader interfaces, d$_0$ = 0.45 nm, did reduce conductivity. Thus, the disruptive effects of roughness and mixing in simulations, currently constrained in the in-plane dimension, may not apply directly to real superlattices with broad islands. An interesting recent study by Termentzidis et al. [126] sought to capture these effects in simulations, revisiting the simplified fcc model for GaAs/AlAs used by Ren et al. while varying both the height and width of interfacial islands. The results reproduce the expected wavelike behavior with defect interfaces and particle behavior with certain roughness, but some unexpected behavior with other rough interfaces. Hence, further work is still required to dissect the problem.

Lattice mismatch has also been shown to play an important role in superlattice thermal conductivity. For example, the Si/Ge system exhibits a mismatch around 4%, and dislocations will form when layers are sufficiently thick. Lee et al. [109] invoked this phenomenon to explain an anomalous dropoff in experimental measurements of k as the period length L increased past about 100 Å. Even without the formation of dislocations, lattice mismatch causes interfacial lattice strain that could potentially affect overall transport. MD simulations by Chen et al. [96] demonstrated a minimum in k versus L for perfect interfaces, but the trend disappeared when the two materials had a 4% lattice mismatch, despite the constituent layers being too thin to form dislocations. The authors suggested that the mere presence of strain must cause sufficiently diffusive interfacial scattering to disrupt coherence.

3.6 Multilayers: Applications and Outlook. Although phonon transport in multilayers and superlattices still holds great potential for further basic research, researchers have gleaned enough insight to apply to the active design of some novel structures. Taken together, these insights show that coherent effects might be important in certain systems, but in practical terms, the direct reduction by interface scattering is easier to exploit. We note two dramatic implementations in reports of fully dense solids designed for ultralow thermal conductivity. Costescu et al. [122] used atomic layer deposition and magnetron sputtering to grow multilayers of W and amorphous Al$_2$O$_3$, which showed the expected decrease of k with interface density and a minimum $k_0$ of 0.6 W m$^{-1}$K$^{-1}$. With a similar approach, Chiritescu et al. [127] measured a conductivity of around 0.05 W m$^{-1}$K$^{-1}$ across layers of WSe$_2$, which were themselves crystalline but stacked with random in-plane orientation. The resulting cross-plane conductivity was at least an order of magnitude lower than in typical amorphous solids [128] due to weak interlayer van der Waals bonding: conductivity actually increased when the layered structure was damaged by ion irradiation. The WSe$_2$ system is perhaps not a multilayer in the typical sense, but it certainly illustrates the strategy of using laminar structures to dramatically suppress thermal transport.

As work continues on multilayer systems, we note that future research should carefully evaluate contributions from size effects, which may be potentially conflated with contributions from the layered structure. Cheaito et al. [129] reported measurements of thermal conductivity in nondilute Si$_{1-x}$Ge$_x$ alloys, showing that size effects (i.e., boundary scattering) actually dominated over alloy scattering, even in films hundreds of nanometers thick. Hence, when evaluating the mechanisms affecting phonon transport in multilayer structures, and particularly when comparing their thermal conductivity to the “alloy limit,” the total sample thickness is likely to have a more important effect than previously recognized.

Thermoelectric materials extend the problem of minimizing thermal conductivity by also requiring high electrical conductivity corresponding to an ideal material that behaves simultaneously as an “electron crystal and phonon glass.” Multilayered structures are one approach for attaining such a material, if the interfaces can be designed to preferentially scatter phonons but not electrons. An interesting illustration of this concept is the “isotopically modulated” $^{28}$Si/$^{28}$Si superlattice, in which Bracht et al. [130] measured a cross-plane thermal conductivity around
one-third that of bulk silicon (with $L \sim 10$ nm). In addition to interest in its inherent properties, the structure also represents a unique analog to common MD simulations of purely mass-varied materials. However, no direct measurement of thermoelectric performance was made. Examples of periodic structures with high reported thermoelectric figures of merit $ZT$ include $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ thin film superlattices [131] and $\text{PbSeTe/PSSTe}$ quantum dot superlattices [132]. The latter example begins to blur our definition of a superlattice, and suggests the broad range of structures that are being studied for thermoelectrics. In a later example, Kim et al. [133] embedded ErAs nanoparticles of various size and spacing in $\text{In}_{0.53}\text{Ga}_{0.47}$As alloy, demonstrating a systematic reduction in $k$ with corresponding increase in predicted $ZT$. Nanocomposite materials are also very promising for this application, with suppressed phonon transport due to high interfacial density as in superlattices. For a detailed discussion of nanocomposites for thermoelectrics, we refer to the review by Minnich et al. [134].

Phase change memory (PCM) is yet another application for engineering reduced thermal conductivity. PCM uses varying pulses of electrical current to switch the state of the recording medium between crystalline and amorphous phases. One strategy to reduce the necessary programming current has been to engineer phase change materials with lower thermal conductivity. For example, compared to typical GeSbTe-type (GST) alloy, Chong et al. [135] demonstrated reduced programming currents in cells based on GeTe/Te$_2$, superlattices, which they attributed largely to reduced thermal conductivity. Tong et al. [119] used $3\theta$ measurements and MD simulations to verify the reduction in thermal conductivity with increasing interfacial density. However, we note that many factors contribute to PCM performance, and thermal properties are only one aspect. Simpson et al. [136] also studied GeTe/Te$_2$ superlattices and demonstrated significantly improved performance over GST, but thermoreflectance measurements showed that thermal conductivity suppression was not a major contributor. Rather, they attributed the performance gains to a minimized difference in configurational entropy between the crystalline and amorphous states, as affected by the layered structure. As the understanding of superlattice properties develops in separate fields, this example demonstrates the importance of more interdisciplinary work. This example also highlights the future potential for synergistic design, in which a system could potentially exploit thermal, electrical, and other effects simultaneously in a single structure, especially at multiple scales.

In the future, even further reductions to thermal conductivity might be attained by precisely manipulating the periodicity (or lack thereof) in multilayer structures. Simulations by Landry et al. [98] and by Franchioni and White, Jr. [102] both suggest that structures with irregular layer thicknesses, while maintaining sharp interfaces, could exhibit conductivities significantly lower than in regular periodic structures. To our knowledge, this strategy has not been explored in systematic experiments. The same strategy was proposed by Lau et al. [137] for suppressing photonic thermal transport, predicting that coherence in an aperiodic system may suppress conductance even more strongly than interface-dominated incoherent transport. Given the findings to date that transport in superlattices and multilayers depends so strongly on interfacial quality, detailed characterization accompanying experimental results is crucial to further understanding. Photoluminescence and Raman scattering are examples of tools that have been used for characterization of interface roughness in superlattices, but not often in direct conjunction with thermal measurements [118]. There are also examples of using transmission electron microscopy to gain useful information about interfaces in superlattice structures [138,139]. Experimental characterization of interfaces could be especially useful when coupled with modeling. Advances in implementations of first-principles methods such as density functional theory (DFT) are enabling modeling of more realistic interfaces, which may help to resolve their effect on coherent transport in experimental measurements.

The question of electron-phonon coupling across metal/insulator interfaces, raised briefly in Sec. 2.8 for single interfaces, is also receiving increasing attention in multilayer systems. For example, very recent reports by Li et al. [140] and Bozorg-Grayeli et al. [141] have investigated the thermal transport in metal/semiconductor Mo/Si multilayers, which have optical properties desirable for extreme ultraviolet lithography. Detailed modeling of such systems is sparse; one example is a report by Mahan [142] in which a continuum-level description was used to calculate cross-plane conductivity. Again, this topic is beyond the scope of this review, but we expect that it will be an area of increasing future research.

Future work could also investigate superlattices in reduced-dimensionality structures. A decade ago, Li et al. [143] reported temperature trends in the conductivity of Si/Co nanowires with diameters as small as 22 nm, finding alloy scattering to be dominant. Much potential for experimental work remains, and models have indicated interesting effects in low-dimensional superlattices. For example, Shiomi and Maruyama [144] simulated the conductivity of isotopically modulated $^{12}$C/$^{13}$C nanotubes, showing a slight minimum in $k$ versus $L$. However, the predicted reduction is relatively small (~40%–50% compared to pure $^{12}$C nanotube) given the anticipated difficulty in fabricating such a system. More recently, Jiang et al. [145] predicted the conductivity of nanoribbon BN/graphene superlattices, which may be somewhat more feasible to produce experimentally. Using a nonequilibrium Green’s function approach, they also reported a minimum with period length. However, in both the nanotube (1D) and nanoribbon (2D) systems, the minimum $k$ occurred with period lengths $L \ll \lambda$, apparently ruling out the transition between particle- and wavelike transport as a cause. The trend is not yet well understood, but suggests that superlattices with reduced dimensionality could be a source of even more interesting transport phenomena related to the control of mode confinement.

## 4 Polyjunctions

We have discussed single interfaces and multilayer materials as well as how their thermal properties scale with various effects such as material composition, temperature, and structure. Nanostructures that lie between the limits of a single interface and the periodic interfaces of a multilayer present additional challenges in terms of modeling. Not only will the interfacial conditions such as roughness and defects influence transport, but the wave nature of phonons must also be considered as in multilayers. Great strides in the understanding of interfacial and multilayer transport have been made in the past decade, and we anticipate that lessons learned thus far will inform modeling approaches to this new regime. We refer to this class of nanostructures as “polyjunctions” owing to the number of materials or interfaces that participate and the engineering purpose of such structures: to join materials while giving increased control over transport properties. The generic structure of a polyjunction is presented in Fig. 4; it consists of two bulk materials joined by $N$ material layers that are on the order of angstroms to nanometers in thickness and selected in order to tune the overall phonon conductance. The thinness of the layers compared to phonon wavelength and mean free path ensures that the system behaves like one indivisible structure instead of a series of isolated interfaces. Here we

![Fig. 4 Schematic diagram of a polyjunction. The material and thicknesses of the N layers are selected to tune the transport. For N = 0, the original interface is recovered.](image-url)
Polyjunction Bridge. It is evident from Eqs. (3) and (4) and the results discussed in Sec. 2.1 that phonon transmissivity is higher between matched materials. Thus, a polyjunction can be used to split an interface between mismatched materials into two (or more) interfaces between better matched materials in an attempt to raise the overall $h_{BD}$. Liang and Tsai [146] investigated the effects on $h_{BD}$ of varying the inserted film bond strength and thickness in a simulation. They found that, for weakly bonded films, a monolayer of the film material provides enhancement, while any more than this will lead to a decrease in $h_{BD}$. Conversely, for a thin film with strong bonds, enhancement is seen across all thicknesses with the maximum values dependent on the bond strength. The degree of enhancement was also dependent on the mismatch between the bulk materials, with a smaller mismatch leading to less enhancement after the thin film was added. In subsequent simulations, Liang and Tsai [147] found that the conductance was maximized for a film having the geometric mean of the Debye temperatures of the interface solids. Overall, a maximum enhancement factor of about 2.5 in $h_{BD}$ was observed. Simulations by English et al. [35] also showed that $h_{BD}$ could be enhanced with the addition of a thin film and that the film should be as thin as possible and have vibrational properties intermediate to the bulk materials. The authors also demonstrated that adding moderate interdiffusion further enhanced $h_{BD}$. Using these methods, $h_{BD}$ was ultimately enhanced by as much as 53% over the original film.

4.2 Polyjunction Barrier. Inserted thin films may also be applied to an originally single material [38,151–153]. In this capacity, the polyjunction acts as a sort of phonon “speed bump.” In wavepacket studies of a LJ/heavy-LJ/LJ system, Tian et al. [152] found that in the long wavelength limit, the transmission was described by the AMM with consideration for constructive/destructive interference effects. For higher wavenumbers, where the barrier material did not contain energy levels that would allow elastic scattering, the wavepacket could tunnel through the barrier via evanescent wave transmission. That is, treating the thin film as a bulk material, the thin film contained complex wavevectors of the correct frequency, leading to exponentially decreasing packet amplitude that survived to the second interface due to the thin nature of the film.

5 Conclusions
In conclusion, we have reviewed the mechanisms of phonon transport across interfaces, multilayers, and polyjunctions in light of recent theoretical, simulated, and experimental findings. For each type of feature, we have emphasized opportunities for tuning thermal transport, which may be harnessed to improve the thermal performance of structures with high interface densities. Realistically, the solution to current thermal challenges lies not with one...
specific approach, but will require device design that simultaneously incorporates thermal transport with other performance criteria. In addition, successful strategies for thermal dissipation or insulation in modern technologies will require the engineering of thermal transport at all available length scales from the bottom up, starting with the nanoscale issues described here.

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Nomenclature

\[ D = \text{spectral phonon density of states, m}^{-3} \text{(rad/s)}^{-1} \]
\[ L = \text{multilayer period length, m} \]
\[ T = \text{temperature, K} \]
\[ Z = \text{acoustic impedance, kg m}^{-2} \text{s}^{-1} \]
\[ a = \text{lattice constant, m} \]
\[ d = \text{layer thickness, m} \]
\[ d_0 = \text{extent of interfacial roughness, m} \]
\[ f = \text{Bose–Einstein distribution function} \]
\[ h = \text{reduced Planck constant, J s} \]
\[ h_{BD} = \text{thermal boundary conductance, W m}^{-2} \text{K}^{-1} \]
\[ k = \text{thermal conductivity, W m}^{-1} \text{K}^{-1} \]
\[ q = \text{heat flux, W m}^{-2} \]
\[ r = \text{interatomic distance, m} \]
\[ u = \text{interatomic interaction energy, J} \]
\[ \nu = \text{phonon group velocity, m s}^{-1} \]

Greek Symbols

\[ \alpha = \text{phonon transmission probability} \]
\[ \varepsilon = \text{Lennard-Jones energy scale, J} \]
\[ \kappa = \text{effective spring constant, N/m} \]
\[ \lambda = \text{phonon mean free path, m} \]
\[ \mu = \text{cosine of phonon incidence angle} \]
\[ \sigma = \text{Lennard-Jones length scale, m} \]
\[ \theta_i = \text{zenith angle of transmitted phonon, rad} \]
\[ \omega = \text{angular frequency, rad s}^{-1} \]
\[ \omega_0 = \text{cut off frequency, rad s}^{-1} \]

Subscripts

\[ j = \text{phonon branch index} \]
\[ 1, 2 = \text{material index} \]

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