Theoretical Paradigm for Thermal Rectification via Phonon Filtering and Spectral Confinement

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A Theoretical Paradigm for Thermal Rectification via Phonon Filtering and Spectral Confinement*

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Significant thermal rectification has the potential to revolutionize approaches to controlled heat flow and enable breakthrough technologies such as phononic computing. We demonstrate a framework based on phonon population confinement and filtering that has potential to reach rectifications that are an order of magnitude larger than previous literature. With the use of a straight-forward modification of the phonon gas model, we illustrate theoretical thermal rectification in a thin-film of diamond (1-10 nm) graded to dimensions $> 1\mu$m of between 25% and 250%. Utilizing this mechanism for thermal rectification sets the stage for significant development in thermal devices.

Introduction.–The development of solid-state thermal device architectures is expected to result in transformative technological breakthroughs similar to those realized in the early development of the microelectronics sector. For instance, thin-film thermal rectifiers have the capacity to revolutionize phonons as information carriers, allowing for the realization of phononic computing [1]. Similarly, thermal biasing is pivotal for improvements in thermal barrier coating effectiveness and heat mitigation in electronic devices [2]. Such biasing has traditionally been achieved either when thermal gradients are sufficiently large to produce corresponding gradations in temperature-dependent thermal conductivity across a set of dissimilar materials [2–7] *or* when there exists mass gradation in the direction of heat flow [8].

Recent work by Chang et al. [9] describes a process to produce thermal rectification via an asymmetric phonon scattering via partial mass loading of amorphous $C_9H_{16}Pt$ particles on the outer surface of a boron nitride nanotube results in a measured thermal rectification of $\sim 7\%$. While asymmetric structuring has yielded interesting laboratory scale results, the magnitude of thermal rectification achieved remains relatively low ($<$ 10-50%) in the absence of significant thermal gradients in the direction of heat flow [4, 10–17]. In fact, the authors are aware of only one study that experimentally demonstrates a thermal rectification ratio well above this [18] by tunnel-coupling metals to superconducting elements. We note, however, the difficulty associated with the integration of such a device into practical thermal applications. In this work, we provide a physical construct that can be used to design thermal rectifiers that do not rely on thermal and/or mass gradients to produce an observable thermal rectification effect.

In contrast to geometric asymmetry and imposed temperature gradients, we highlight the conditions necessary for thermal rectification from the perspective of available wavelengths in the phonon density of states as thermal energy traverses thin-film material stacks in opposing directions. The mechanism proposed in this work focuses strictly on phonon filtering via spectral confinement. In essence, if a portion of the available bulk phonon spectrum is limited by dimensional confinement and the confined spectrum propagates heat through a subsequent layer of the same material, the limited spectrum should conduct heat less effectively. In other words, the amount of heat that can be carried through a material after first passing through a phonon filter is less than if the heat traveled through the unfiltered medium first. We show that, under specific conditions, thin film/thick film bi-layers and graded thin films can lead to a filtering effect where the total heat carrying population going from thick to thin is greater than going from thin to thick. We therefore describe this phenomenon as thermal rectification enabled by phonon filtering using spectral confinement.

Modeling thermal rectification via phonon confinement.– While there exist a number of computationally intensive modeling techniques that would demonstrate this rectification effect, we choose to utilize an experimental phonon dispersion to evaluate the analytical phonon gas model put forward by Callaway [19, 20].

$$C_v = \frac{1}{2\pi^2}\sum_j \int_k \hbar\omega \frac{\partial f_{BE}}{\partial T} k^2 dk \tag{1}$$

and,

$$\kappa = \frac{1}{3}\sum_j \int_{k_{min}}^{k_{max}} C_v \nu \left[l_{in}^{-1} + l_{bound}^{-1}\right]^{-1} dk \tag{2}$$

where κ and C_v are thermal conductivity and volumetric heat capacity, respectively. In the above expressions, j represents the polarization index, ν the phonon group velocity, ω the angular frequency, k the wavevector and $\frac{\partial f_{BE}}{\partial T}$ the temperature derivative of the Bose-Einstein distribution.

The phonon mean free path, l is incorporated into the physical representation of thermal conductivity to account for energy carrier scattering. This is done using Matthiessen's rule, which allows us to isolate the intrinsic phonon mean free path, l_{in}, and the boundary limitation to the mean free path, l_{bound}. In this work, we limit our analysis to one-dimensional heat flow across thin film configurations. Thus, l_{bound} is treated as the characteristic length, or thickness, of an individual film.

This integral is taken over the available wave vector space from $k_{min} = \pi/d$ to $k_{max} = 2\pi/a$, where d is the physical dimension of the crystal (or treated as infinite, with a negligible minimum wave vector, for an ideal bulk formulation) and a is the lattice constant of the crystal. Despite its simplicity, this model captures the effect of thermal rectification via multi-layer phonon filtering in a way that demonstrates its impact on a material's total thermal conductivity. Please see the Supplemental Material [URL] for further discussion on the appropriateness of the use of the Callaway model within the context of phonon transport through thin films at nanometer length-scales

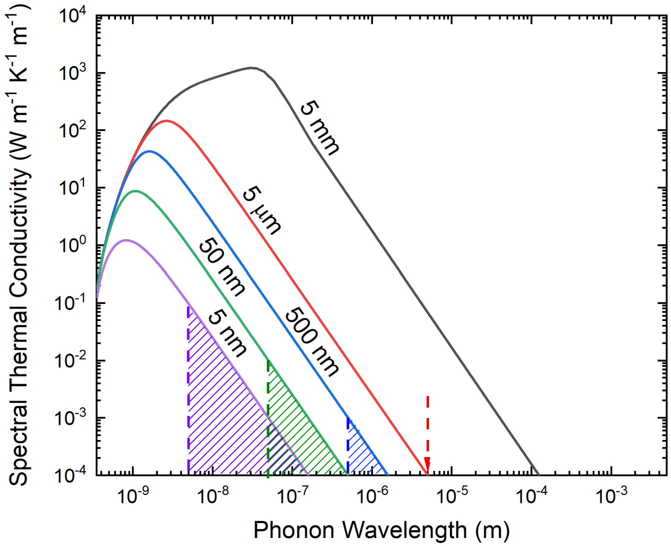

FIG. 1: **Diamond spectral thermal conductivity vs. phonon wavelength from a typical scattering-limited thin film model. Curves are included for samples with thicknesses of 5 mm (black), 5μm (red), 500 nm (blue), 50 nm (green) and 5 nm (purple). Also included are dashed lines indicating where the wavelength of phonons corresponding to the film thickness lies. Phonons with wavelengths greater than the film thickness (shaded with diagonal lines where they appear in the figure) contribute far less than the primary heat carrying phonons.**

[19–22].

Typically, the impact of nanostructuring on thermal conductivity is assumed to be accounted for entirely by modifications to the phonon mean free path. With regards to phonon population confinement, it is useful to consider spectral contributions to the thermal conductivity, shown in Fig. 1 for diamond films of various thickness. Here the impact of nanostructuring on thermal conductivity is done solely using a mean free path that is limited by boundary scattering. This spectral analysis provides valuable insight into the effect that a given population of phonons has on the total thermal conductivity. This has been addressed within the wider literature, most notably through the concept of mean free path accumulation [23–28]. A significant point of physical insight gained by this analysis is that the peak population of phonons have a significantly smaller wavelength than the film's characteristic dimension, and is further reduced as the sample dimension shrinks.

In terms of relative contributions, the peak phonon wavelength contributes orders of magnitude more to the thermal conductivity than wavelengths that are near the film thickness. To illustrate this point, the characteristic boundary dimension is plotted in Fig. 1 with a dashed, vertical line for each film thickness (or the bounds of the figure for the 5 mm film). In the context of *phonon filtering*, boundary scattering preferentially eliminates (or filters out) contributions to the thermal conductivity from phonons that are greater than the film thickness. As a consequence of the relatively low contribution to the thermal conductivity made by phonons having wavelengths greater than the film thickness, we assert that these dimensions can be considered as the predominant confining features of the material. In fact, in a free standing nanostructured system, the confinement of available phonons is clearly reduced to the nanostructured dimension and incorporation of longer wavelength phonons that are even available to undergo scattering would be *non-physical* [29, 30].

We examine the impact of treating those boundaries, previously considered only as scattering sites, as sites that

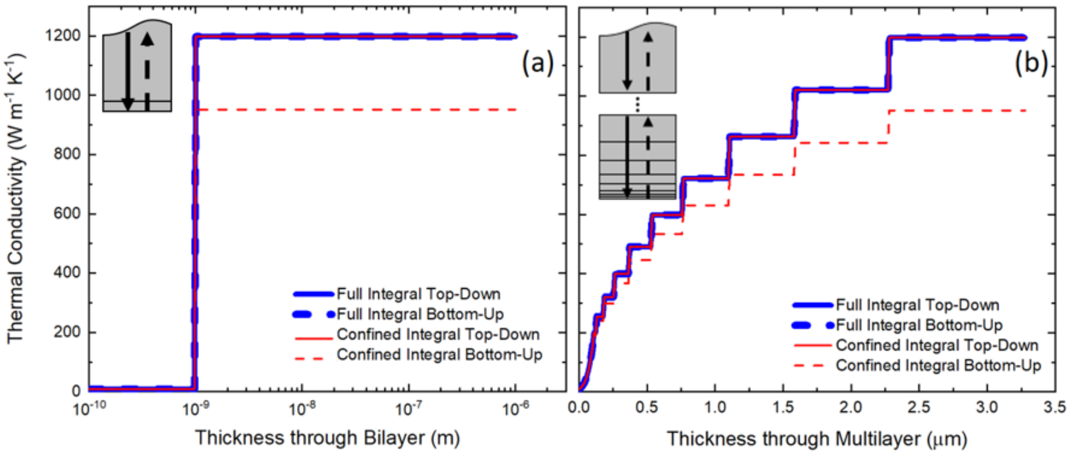

FIG. 2: **Thermal conductivity of diamond through the thickness of a bilayer (a) and multilayer (b) film from the bottom side of the film stack up (thin to thick, dashed lines), and the topside down (thick to thin, solid lines). Models are shown using the scattering limited modeling (thick blue line and dashes, no directional difference) and the confined phonon population model (red line and dashes). Top-down, both modeling approaches match. However, bottom up, the confined phonon model results in a limited thick-film thermal conductivity due to a lack of long wavelength phonons in the incoming phonon population. This results in a significant difference in thermal conductivity and large thermal rectification effects. To clarify the bilayer and multilayer configuration, cartoons are provided inset with arrows indicating heat flow direction.**

confine the population of phonons available to transfer thermal energy across a layered system. This implies that the maximum available phonon wavelength (i.e. the lower bound of our integration in wave vector space) is governed by the characteristic dimension of the nanostructured component. For a free standing film with one dimensional heat flow, the film thickness (t) serves as the relevant dimension for phonon confinement.

In order to account for possible phonon confinement effects in our model, we modify the bounds of our integration such that we disregard wave vectors below $k_{min} = \pi/t$. This simple approach to redefine the available phonon spectrum provides for a more rigorous treatment of the physics that govern thermal transport in multi-layer nanoscale films, and allows for an additional mechanism to achieve thermal rectification in multi-layer material systems.

We validate our confined phonon model by comparing computations of temperature-dependent thermal conductivity for single-layer diamond films to those obtained by integrating across all phonon wavelengths using literature values for the parameters in Eq. 2. Seen in the supplemental information, both models match well and are found to be consistent with those values available in literature [23, 31–35].

Thermal rectification in nanostructured bi-layers and multilayers.–In order to use a phonon confinement effect to achieve thermal rectification, layered (or graded) structures must be fabricated such that a confined phonon population can be injected from one layer into an otherwise non-confined layer, thus using the confined layer as a phonon filter. We consider two configurations that each represent a free-standing membrane where heat could be injected from either side: a bi-layer (thin-film on thick film) and a graded multilayer.

For the available phonon population to remain consistent on opposing sides of the film boundary, the interface between the phonon filter layer and adjacent thick layer(s) must not be completely diffusive. If the morphology of the interface results in diffuse and anharmonic phonon scattering, then the transport of thermal energy from one film to the other would result in a redistribution of phonons that assumes the thick film's enlarged density of states, rendering this formulation invalid. The idea of a harmonically scattering interface, which scatters phonons effectively but does not alter the injected phonon population, is critical to the physical mechanism for phonon filtering discussed here. There are a variety of examples of real materials which contain interfaces that are nearly ideal, such as nanocrystalline diamond with twinned grain boundaries [36], Si-based superlattices [37], and multilayers grown with remote epitaxy [38]. Implementation of near-ideal interfaces for our mechanism of confined phonon filtering will serve not only to further motivate exploration of these types of boundaries, but may also serve to validate potential fabrication methods that aim to achieve a perfect harmonically scattering interface.

Likewise, this thermal rectification mechanism requires a lack of redistribution of the phonon population from anharmonic phonon scattering within each layer itself. While anharmonicity effects are taken into account in the intrinsic mean free path within our model, we assume that the phonons injected into the thick film from the filter layer do not scatter anharmonically into wavelengths that may not have been available to begin with. This idealization is closest met by phonon thermal conductors with high thermal conductivity and low anharmonic phonon scattering such as diamond, GaN, BAs, and hBN [39–42].

Provided these requirements are met, this treatment can be used to design a solid-state thermal rectifier using multilayer thin-films. The most palpable system to imagine is a bilayer membrane having one ultra-thin layer below a thick layer. In Fig. 2a we provide an example of thermal rectification in a bilayer diamond film system that consists of a 1 μm film above a 1 nm film. The thermal conductivity is not directionally dependent when calculated using mean free paths that are limited by boundary scattering only (as expected). Conversely, the phonon confinement analysis *does* yield a directionally-dependent thermal conductivity. When we apply these physics to the case when heat flows from the thick film to the thin film, the confined thermal model results in a thermal conductivity distribution identical to that obtained from the "full integral" model. However, if heat flows in the reverse direction, we obtain a significantly reduced thermal conductivity in the thick layer since we are not fully populating all available phonon modes. The directional-dependence of thermal conductivity results in significant thermal rectification.

Mathematically, the resulting thermal rectification originates from modifications to the limits of integration in Eq. 2. Considering the case when heat emanates from the thick-film side, $k_{min} = \pi$ μm^{-1} (as well as $l_{bound} = 1$ μm), which then become limited in the thin film portion of the stack. In the opposing direction, however, $k_{min} = \pi$ nm^{-1} (and $l_{bound} = 1$ nm). Even though the mean free path is relaxed as the heat moves into the thick layer ($l_{bound} = 1$ μm), k_{min} does not change and so the confinement results in diminished thermal transport from the filtered phonon population.

We also examine these physics in the case of a 20 layer material stack with logarithmically increasing thickness (in this case, ranging from 1 nm to 1 μm). This is the type of dimensional evolution that one might see from nucleation and grain growth in a typical top-down film deposition technique [36]. Here, our confinement still originates from the initial filtering layer (1 nm). We again note that this model assumes that no anharmonic interactions occur, however, traversing this many interfaces in a real material system would inevitably lead to some redistribution of phonon population. Nevertheless, this provides an upper limit to thermal rectification (in the absence of any external temperature gradient or material asymmetry).

A thermal rectification ratio, TR, is used to calculate the degree of thermal rectification achieved relative to other

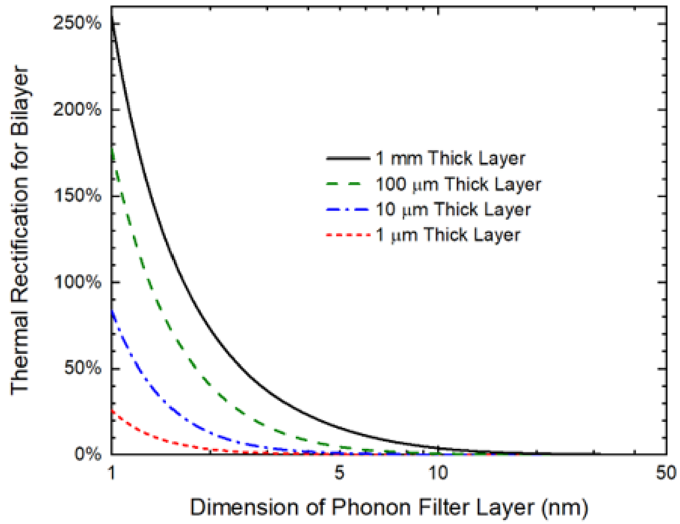

FIG. 3: **Thermal rectification over various phonon filter dimensions (i.e. the thin layer in the bilayer) for diamond films by the confined phonon population model. Various dimensions of the thick film demonstrate that thermal rectification becomes more extreme with greater disparity between the filter layer and the top layer.**

works [8, 14] and is represented by,

$$TR = \frac{\kappa_{TD} - \kappa_{BU}}{\kappa_{BU}} \tag{3}$$

where κ_{TD} is the thermal conductivity with heat moving from the top down and κ_{BU} is the thermal conductivity from the bottom up.

The thermal rectification ratio is plotted for the bilayer system over various phonon filtering layer thicknesses in Fig. 3. In this formulation we compare the directional thermal conductivities in the thick layer only as it represents the largest thermal resistor in the bilayer. We also include distributions for a number of different thick layer length scales. Physically, thick layers with less boundary scattering are at greater risk for diminished thermal conductivity due to phonon confinement. However, even in a bilayer that consists of a 1 μm film with a 1 nm filter layer, the thermal rectification ratio is $> 25\%$. We note that this is considerably higher than thermal rectification ratios that have been reported in literature (for cases where a large temperature gradient across the structure is absent). In the case where there is significant dimensional mismatch, extremely large thermal rectification ratios can be achieved ($> 250\%$). The upper range of these thermal rectification ratios is expected to revolutionize a wide range of thermal devices and facilitate the development of phononic computing.

This mechanism for thermal rectification will hold preferentially when the filtering layer is on the order of the peak thermal conductivity contributors from the phonon spectrum. This is demonstrated by our model in Fig. 3; when the filter layer thickness is greater than $\sim$10 nm, thermal rectification is negligible. As the peak contributors to the thermal conductivity exist in the sub-10 nm range (particularly in the thin film regime), that is the regime where we expect to see significant effects of phonon confinement.

When multiple layers are present, the thermal rectification ratio is computed using average directional thermal conductivities in Eq. 3. This results in a thermal rectification ratio that is slightly reduced (17% in the 20 layer system that goes from 1 nm to 1 μm compared to 25% in the same extremes for a bilayer). Additionally, we do not consider thermal boundary resistances in our rectification calculation. As typical temperature increases across intimately contacted interfaces are less than a few kelvin [43], we do not expect the boundary resistance to alter the effects of the phonon population confinement from the layers themselves.

Discussion.– The use of a phonon filter layer to confine a population of phonons across a thin-film boundary is extremely promising for the realization of effective thermal rectifiers. This physical mechanism enables thermal rectification in realistic devices with sample configurations that can be readily integrated into microelectronics processing techniques. Extreme thermal rectification ratios are predicted, which will finally allow for robust experimental demonstrations of thermal rectification.

We have studied a novel physical mechanism for thermal rectification via phonon filtering. This can be modeled simply by modifying a phonon gas formulation for thermal conductivity. To realize thermal rectification, we have extended our physical treatment by considering the confinement of phonons when film thickness is sufficiently small. By restricting the integration limits to the characteristic dimension of a film, we can estimate the impact of phonon confinement on the density of phonon states available for thermal transport while simultaneously capturing the phonon filtering effects that are well-known within the scientific community. This can be extended to multilayer, graded materials, which are an important class of materials for integration into larger system platforms.

Though this analysis relies on a lack of anharmonic interactions across interfaces and within each material layer, it does provide a new mechanism that can be used to determine an upper limit to thermal rectification that can be achieved in an ideal system. In diamond (a material that does, in fact, demonstrate low anharmonic scattering [31]), this upper limit is computed to be ∼250%, which is orders of magnitude larger than any experiments yet to be reported in literature. As this mechanism is distinct from other thermal rectification approaches such as thermal gradients driven by geometrical asymmetry or extrinsically imposed boundary conditions, there is potential to even further realize thermal rectification in actual devices when multiple mechanisms are combined. Even if a fraction of this limit should be realized experimentally, it would allow for the production of practical thermal devices and represent a major advancement in the thermal sciences.

Utilization of phonon confinement and filtering for thermal rectification sets the stage for various experimental and theoretical work to optimize the implementation of this approach. For instance, the optimization processing and materials constituents could lead ideal boundaries that yield rectification ratios laid out in this work. Additionally, there remains a question of the magnitude of within-layer harmonicity lengths that would determine an ideal thickness in the host (non-filter) layer of a bi-layer system. While it would not change the physical concept behind this mechanism, determining the effectiveness of phonon filtering on individual phonon mode characteristics (wavelength, group velocity, etc.) could have a significant impact on the full realization of this mechanism as well. A combination of fundamental modeling and careful experimentation will help to develop the realization of this mechanism and enable its incorporation into revolutionary new devices that are expected to enable applications such as advanced thermal barriers, smart heat sinking, and phononic computing.

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