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Rationalizing phonon dispersion for lattice thermal conductivity of solids

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ABSTRACT

Lattice thermal conductivity (κ_L) is one of the most fundamental properties of solids. The acoustic–elastic-wave assumption, proposed by Debye (Debye P. *Ann Phys* 1912; **344**: 789–839), has led to linear phonon dispersion being the most common approximation for understanding phonon transport over the past century. Such an assumption does not take into account the effect of a periodic boundary condition on the phonon dispersion, originating from the nature of periodicity on atomic arrangements. Driven by modern demands on the thermal functionality of materials, with κ_L ranging from ultra-low to ultra-high, any deviation from the Debye approximation in real materials becomes more and more significant. This work takes into account the periodic boundary condition, and therefore rationalizes the phonon dispersion to be more realistic. This significantly improves the precision for quickly predicting κ_L without any fitting parameters, as demonstrated in hundreds of materials, and offers a theoretical basis rationalizing κ_L to be lower than the minimum currently accepted based on the Debye dispersion. This work paves the way for designing solids with expected κ_L and particularly inspires the advancement of low-κ_L materials for thermal energy applications.

Keywords: thermoelectric, thermal conductivity, minimal thermal conductivity, phonon dispersion

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INTRODUCTION

Lattice thermal conductivity (κ_L) strongly affects the applications of materials related to thermal functionality, such as thermal management [1], thermal barrier coatings [2] and thermoelectrics [3–5]. κ_L is determined by the specific heat (c_V), phonon group velocity (v_g) and phonon relaxation time (τ), which are all strongly linked to the dispersion of phonons. By manipulating these physical parameters, many different materials either with ultra-low or ultra-high κ_L have been successfully made [6–8].

In cases of applications that require a low κ_L, such as thermoelectrics, complex crystal structures are usually focused on. This is because an increase of the number of atoms in a primitive cell folds the high-frequency portion of phonons back into the first Brillouin zone as optical ones with significantly reduced group velocities. This reduces the fraction of acoustic phonons, which is equivalent to the effect of reducing the acoustic specific heat for κ_L-reduction, since acoustic phonons are the dominant contributors to κ_L because of their high group velocities [8–12]. Alternatively, both introducing defects with different dimensionalities (0D point defects [13–17], 1D dislocations [18–21] and 2D interfaces [22,23]) and utilizing the strong lattice anharmonicity [24–27] help to shorten the overall phonon relaxation time (τ). In addition, a weak bonding force in materials with heavy elements leads to a small slope of phonon frequency versus wave vector, meaning a small group velocity (v_g) for phonons [28,29].

In cases of applications that require a high κ_L, carbon materials such as 3D diamond [30], 2D graphene [31] and 1D carbyne in the form of cumulene [32] have strong C–C chemical bonds, light atomic mass and small primitive cells and therefore show the highest κ_L among known solids.

In order to understand the lattice thermal conductivity more quantitatively and in a time- and cost-effective way, many researchers devoted their efforts to it and developed a few physical models using approximated phonon dispersions over the past century [33–45] (see the supplementary section entitled 'Development of modeling lattice thermal

conductivity'). Most [33–40,45] of these models use a linear phonon dispersion, as proposed by Debye in 1912 based on an acoustic–elastic-wave assumption [46], while other models either involve mathematical fitting parameters on phonon dispersion [41–43] or lack detailed equations for phonon transport properties [44]. The linear phonon dispersion of Debye offers many simplifications on phonon transport properties, and was the most common approximation in the past. The Debye dispersion successfully predicts a T^3 dependence of the heat capacity (C_V) at low temperatures and C_V approaches the Dulong–Petit limit at high temperatures.

However, the nature of periodicity on atomic arrangements leads to a periodic boundary condition for lattice vibrations in solids, which actually creates lattice standing waves at Brillouin boundaries. This does not satisfy the acoustic–elastic-wave assumption of Debye, as proposed by Born and von Karman (BvK) in 1912 [47]—the same year that Debye proposed the linear dispersion [46]. This results in a significant deviation of Debye dispersion for periodic crystalline materials when phonons with wave vectors are close to the Brillouin boundaries (high-frequency phonons; see the supplementary section entitled 'Detailed deduction on phonon transport properties'). When these phonons are involved for phonon transport (i.e. at not extremely low temperatures), Debye dispersion leads to an overestimation of lattice thermal conductivity because of the overestimation of the group velocity for these high-frequency phonons, as observed in materials with known measured κ_L and necessary details for a time- and cost-effective model prediction to our best knowledge (Fig. 1g and h show a mean absolute deviation of +40% and 35%). In addition, Debye dispersion overestimates the theoretically available lower bound of lattice thermal conductivity ($\kappa_{L,min}$) as well, leading the violations of the measured κ_L to be even lower than the $\kappa_{L,\,min}$ predicted (Debye–Cahill model) [48] to be observed in tens of materials (Fig. 2).

This work takes into account the BvK boundary condition [47], and reveals that the product of acoustic and optical dispersions yields a sine function (see the supplementary section entitled 'Detailed deduction on phonon transport properties'). In the case in which the mass (or the force constant) contrast between atoms is large, the acoustic dispersion tends to be a sine-function (Fig. S1). This sine-type dispersion indeed exists in both the simplest [32] and the most complex materials [49] (see the supplementary section entitled 'Detailed deduction on phonon transport properties'). Approximating the acoustic dispersion to be sine, the BvK boundary condition subsequently reduces the remaining optical branches to a series of localized modes with a series of constant frequencies. It should be noted that, with the development of computation technology, first-principles calculations could enable a more detailed phonon dispersion. However, this is usually time-consuming and computationally expensive, particularly for materials with imperfections. It is therefore still significant nowadays if a rationalized phonon dispersion is developed for a time- and cost-effective prediction of phonon transport.

This work utilizes the above-mentioned rationalization of phonon dispersion, which enables both contributions to κ_L of acoustic and optical phonons to be included. This improvement in phonon dispersions significantly improves the accuracy of a time- and cost-effective prediction on κ_L of solids (Fig. 1c, showing a mean absolute deviation of only ~2.5%), and therefore offers a more precise design of solids with expected κ_L. Furthermore, this work successfully removes the contradiction of the measured κ_L being even lower than the minimum ($\kappa_{L,\,min}$, predicted based on a Debye dispersion, Fig. 2). This would provide the theoretical possibility of rationalizing κ_L to be lower than is currently thought, opening further opportunities for advancing thermally resistive materials for applications, such as thermoelectrics.

RESULTS AND DISCUSSION

The similarity between the linear dispersion proposed by Debye and the one developed in this work lies in the region of acoustic phonons having low frequencies (wave vectors close to the Brillouin zone center, the Γ point). This leads both dispersions to predict a T^3 dependence of heat capacity (C_V) at low temperatures (Fig. S3). The overall phonon frequency from a linear dispersion is higher than that from the dispersion developed in this work, which reduces the probability of phonons being excited and therefore leads to a lower C_V, particularly at mid-temperatures (Fig. S3). In the high-temperature limit, available phonons of any dispersions are completely excited, leading the energy carried by each atom to be $3k_BT$ (known as the Dulong–Petit law, Fig. S3) in bulk solids [50] excluding those with liquid-like species [51,52].

The most successful models without any fitting parameters for a time- and cost-effective prediction of the intrinsic κ_L (with Umklapp scattering only) of crystalline solids are those developed by Slack in 1973 [53], with improvements by Klemens [54], and by Snyder in 2011 [45]. Both models are based on a linear phonon dispersion of Debye for acoustic phonons, and are therefore called

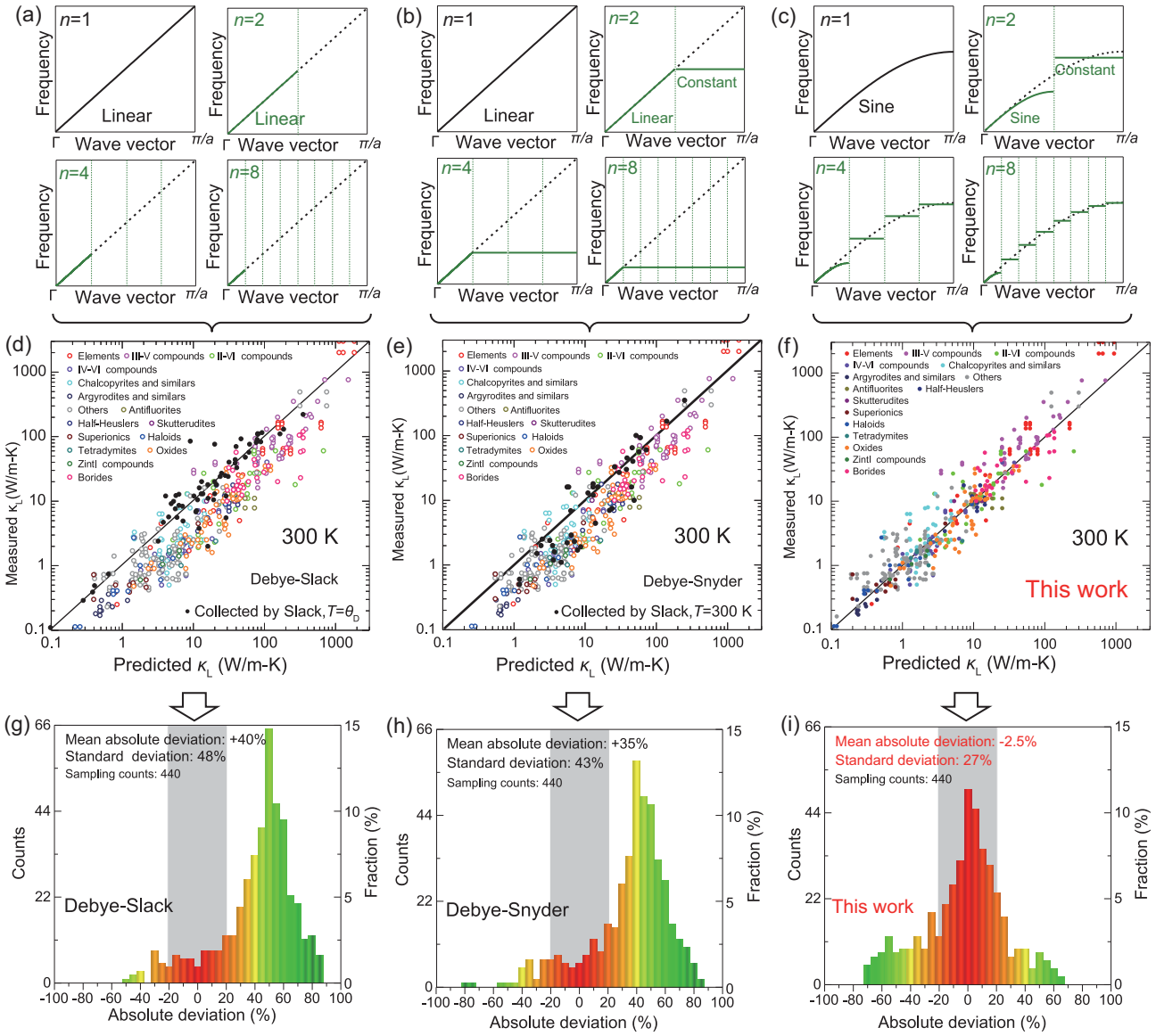

Figure 1. Comparison of phonon dispersion (a, b and c), measured lattice thermal conductivity versus prediction (d, e and f) and the corresponding error analyses (g, h and i) for the Debye–Slack model (a, d and g), the Debye–Snyder model (b, e and h) and the one developed in this work considering the periodic boundary condition (c, f and i) for crystalline solids. Details of the materials involved are given in Table S1.

in this work the Debye–Slack and Debye–Snyder models, respectively. The difference between them is that Slack only considers the contribution of acoustic phonons (Fig. 1a) while Snyder assumes that all optical phonons have the cut-off frequency of the acoustic branch (Fig. 1b). The phonon dispersion developed in this work, taking into account the periodic boundary condition, is shown in Fig. 1c.

In order to better evaluate the accuracy of each time- and cost-effective model prediction to the best of our ability, a total of ∼450 measured room-temperature lattice thermal conductivities from ∼300 different materials are collected for comparison (similar results for other temperatures can be expected since they strictly follow a T^{-1} dependence due to Umklapp scattering; see the supplementary section entitled 'Comparison on κ_L predicted by a Debye-Snyder model and the one developed in this work'). In the case of a linear dispersion, both the Debye–Slack (Fig. 1d) and Debye–Snyder (Fig. 1e) models statistically overestimate κ_L (by ∼37%, Fig. 1). This work successfully enables a removal of such a κ_L-overestimation (Fig. 1f). This can largely be understood by the overestimated acoustic phonon group velocity (particularly at high frequencies; see the supplementary sections entitled 'Comparison on κ_L predicted by a Debye-Snyder model and the one developed in this work' and 'Discussion on $\kappa_{L,min}$-

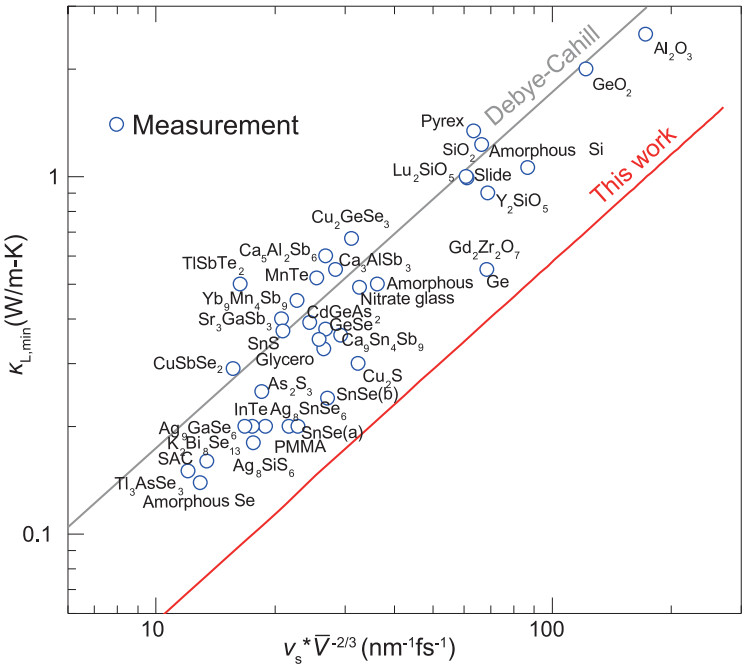

Figure 2. Comparison of measured minimal lattice thermal conductivity ($\kappa_{L,min}$) and predictions based on a dispersion developed according to the periodic boundary condition or on a linear dispersion of Debye (Debye–Cahill model). Details of the materials involved are given in Table S1.

prediction') in the Debye–Slack and Debye–Snyder models, since acoustic phonons are the main contributors to κ_L [8,55].

In statistics (see the supplementary section entitled 'Comparison on κ_L predicted by a Debye-Snyder model and the one developed in this work'), based on a linear dispersion of Debye and further including the contribution of optical phonons (Fig. 1b), Snyder's model reduces both the mean absolute deviation (MAD) and the standard deviation (SD) by 5% statistically, as compared to Slack's (Fig. 1g and 1h). This improvement indicates a weak contribution from optical phonons in general. This work successfully reduces MAD to be about zero (-2.5%, Fig. 1i), indicating that the phonon dispersion developed here indeed takes the major responsibility for κ_L-prediction. Such a significant improvement mostly comes from the development of the dispersion of acoustic phonons (sine versus linear), since all the models use the same scattering parameter (Grüneisen parameter, Table S1) and predict nearly the same heat capacity at high temperatures (Fig. S3).

The remaining SD of ~27% (reduced from ~48%) in this work can be understood largely by the uncertainty of the Grüneisen parameter (γ), measuring the strength of inherent Umklapp scattering. Its estimation can show a variation of 100% or higher from different sources even for a given material (Table S1), meaning a possible error as high as a factor of 4 or more for κ_L-prediction. This opens to the field the importance of the accuracy of γ-determination [24]. This work includes all available γ to the best of our knowledge from the literature on κ_L-prediction (Figs 1 and S4). However, if γ is unavailable, it is assumed to be 1.5, which is a statically averaged γ for known materials (Fig. S4). Note that usage of only the measured Grüneisen parameters from the available literature indeed enables a better prediction (Fig. S4 in the supplementary section entitled 'Detailed deduction on phonon transport properties').

In addition to inherent Umklapp scattering in solids, electron–phonon scattering resulting from a high carrier concentration (particularly in metal/semi-metals and extremely heavily doped semiconductors) as well as resonant scattering (in e.g. filled skutterudites and clathrates) can lead to a significant reduction in κ_L. Once the phonon relaxation time of this type of scattering is known, κ_L of these materials could be reasonably predicted as well, according to the model developed in this work.

As an extreme case of super-large n, typically meaning a super-big primitive cell, κ_L is expected to be extremely low [8,9], which is similar to the case of amorphous solids [48,56]. It should be noted that amorphous solids may show a reduced sound velocity and an enhanced phonon scattering for a lower κ_L as compared to those of crystalline ones, which can be understood by the existence of a distribution in interaction force resulting from the random atomic distance (see the supplementary section entitled 'Sound velocity of amorphous solids').

Based on the phonon theory, when the scattering probability of phonons reaches its maximum, the relaxation time is minimized as half of the period of each phonon [57], leading to a minimal lattice thermal conductivity ($\kappa_{L,min}$). In 1989 Cahill [48] developed a model for predicting $\kappa_{L,min}$ based on a linear dispersion of Debye (the Debye–Cahill model), which is the most common model for a time- and cost-effective $\kappa_{L,min}$-prediction. Due to a similar reason of an overestimation of the phonon group velocity (particularly at high frequencies in a linear dispersion), tens of materials contradictorily show a measured temperature κ_L being even lower than $\kappa_{L,min}$ predicted by this model (Fig. 2; its n-dependence is discussed in the supplementary section entitled 'Detailed deduction on phonon transport properties'). It should be noted that v_s and $\overline{V}$ are respectively the sound velocity and average atomic volume, and the product $v_s{}^*\overline{V}^{-2/3}$ is the key parameter determining $\kappa_{L,min}$ (see the supplementary section entitled 'Collective equations and mathematic code for κ_L-prediction in this work') [48]. With the phonon

dispersion developed here, this work nicely eliminates the above contradiction.

CONCLUSION

Taking into account the periodic boundary condition, a phonon dispersion and thus a time- and cost-effective phonon transport model are developed in this work, which significantly improves the accuracy for quickly predicting the lattice thermal conductivity (κ_{L}) of solids. This offers an effective design for thermal functional solids. It further provides the theoretical possibility of κ_{L} being lower in many materials than is currently thought, validating further potential for advancing the thermal functionalities and thermal energy applications of solid materials.

METHODS

Here we show brief deductions on phonon dispersion and transport properties taking into account the periodic boundary condition [47] (more details are given in the supplementary sections entitled 'Detailed deduction on phonon transport properties' and 'Comparison on κ_{L} predicted by a Debye-Snyder model and the one developed in this work'). Considering the nearest-neighboring interactions, the phonon dispersion of a 1D single-atom chain is strictly a sine function (Equation S1a). Once the number of atoms in a primitive cell (n) and the dimensionality of the material (d) increase, the product of acoustic and optical dispersions yields a sine function (Equation S1b). This leads the dispersion of the acoustic branch to quickly approach a sine function when the mass and/or force contrast is large.

It is therefore reasonable to approximate the acoustic dispersion (frequency of $\omega_{\mathrm{a},j}$ versus wave vector k) for a material with a sound velocity of $v_{\mathrm{s},j}$ (Equation S4) as

$$\omega_{\mathrm{a},j}(k) = \frac{2}{\pi} v_{\mathrm{s},j} k_{\mathrm{c}} \sin\left(\frac{\pi}{2}\frac{k}{k_{\mathrm{c}}}\right), \qquad (1)$$

where j defines the polarizations of lattice vibrations (longitudinal or transverse) and k_{c} is the cut-off wave vector. In the case of $n = 1$, there is no optical branch, and the acoustic branch strictly has a dispersion of sine [47] (Fig. 1c). This means that the phonon group velocity (v_{g}, the slope of phonon frequency versus wave vector) is strongly frequency-dependent, which is further related to the sound velocity (v_{s}) via Equation 1 (see the supplementary section entitled 'Detailed deduction on phonon transport properties'). For simplicity the force constant and atomic mass are both averaged in this work (see the supplementary section entitled 'Detailed deduction on phonon transport properties'). This leads the phonon dispersion (frequency of $\omega_{\mathrm{o},i,j}$ versus wave vector k) of each optical branch to have a series of constant frequencies when $n>1$ (Fig. 1c). Both $\omega_{\mathrm{o},i,j}$ and the effective group velocity ($v_{\mathrm{eff},i}$) are believed to be the ones at the median of wave vectors in the ith extended Brillouin zone for $n = 1$, since the case of $n = \infty$ is the quantization of $n = 1$ (Fig. 1c and the supplementary section entitled 'Detailed deduction on phonon transport properties'). Note that a better understanding of phonon transport can be expected if the detailed dispersions on optical phonons are known (such as by first-principles calculations or inelastic neutron scattering measurements). The resulting equations for specific heat are given in the supplementary material (see the supplementary section entitled 'Detailed deduction on phonon transport properties').

At room temperature or above, the scattering of phonons is known to be dominated by inherent Umklapp processes due to the lattice anharmonicity in most solids. Considering this type of scattering only, the resulting relaxation time (τ_{U}; see the supplementary section entitled 'Detailed deduction on phonon transport properties') enables a determination of lattice thermal conductivity due to acoustic phonons via

$$k_{\mathrm{L,a}} = \frac{1}{d} c_{\mathrm{V,a}} v_g^2 \tau_{\mathrm{U}}. \qquad (2)$$

A constant frequency (i.e. flat dispersion) for each optical branch validates the approximation as the Einstein mode [57], leading the relaxation time to be half of the period (τ_{min}) of each phonon (see the supplementary section entitled 'Detailed deduction on phonon transport properties'). This results in an optical lattice thermal conductivity ($\kappa_{\mathrm{L,o}}$) of

$$k_{\mathrm{L,o}} = \sum_{i=2}^{n} \frac{1}{d} c_{\mathrm{V,o},i} v_{\mathrm{eff},i}^2 \tau_{\mathrm{min,o},i} \qquad (3)$$

and a total lattice thermal conductivity (κ_{L}) of $\kappa_{\mathrm{L}} = \kappa_{\mathrm{L,a}} + \kappa_{\mathrm{L,o}}$

When the scattering of acoustic phonons is maximized, the relaxation time is minimized to be half of the period of each phonon as well. This enables a prediction of minimal lattice thermal conductivity ($\kappa_{\mathrm{L,min}}$).

SUPPLEMENTARY DATA

Supplementary data are available at *NSR* online.

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