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Minimum thermal conductivity in the context of *diffuson*-mediated thermal transport

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A model for the thermal conductivity of bulk solids is proposed in the limit of diffusive transport mediated by diffusons as opposed to phonons. This diffusive thermal conductivity, κ_{diff}, is determined by the average energy of the vibrational density of states, $\hbar\omega_{avg}$, and the number density of atoms, n. Furthermore, κ_{diff} is suggested as an appropriate estimate of the minimum thermal conductivity for complex materials, such that (at high temperatures): $\kappa_{diff} = \frac{n^{\frac{1}{3}}k_B}{\pi}\omega_{avg} \approx \kappa_{min}$. A heuristic finding of this study is that the experimental ω_{avg} is highly correlated with the Debye temperature, allowing κ_{diff} to be estimated from the longitudinal and transverse speeds of sound: $\kappa_{diff} \approx 0.76 n^{\frac{2}{3}}k_B\frac{1}{3}(2v_T + v_L)$. Using this equation to estimate κ_{min} gives values 37% lower than the widely-used Cahill result and 18% lower than the Clarke model for κ_{min}, on average. This model of diffuson-mediated thermal conductivity may thus help explain experimental results of ultralow thermal conductivity.

Broader context

Thermal conductivity of materials is of practical engineering importance. Estimating how low the thermal conductivity can be engineered can set practical limits for a variety of applications. Heat that is transported by the vibrational energy of atoms in a solid can be defined from different perspectives. We typically think of atomic vibrations travelling in waves that we call phonons, the strict definition of which requires the translational symmetry of perfect crystals. However, low thermal conductivity materials are typically full of many types of disorder and defects: from impurity atoms and solid solutions to dislocations, grain boundaries and other interfaces. Alternatively, we may consider the transport of heat by diffusons, which are atomic vibrations that carry heat by diffusion. Diffusons are present in all materials, without the structural conditions required by phonons. It follows that diffusons may better describe the physics of heat transfer in low thermal conductivity materials, particularly at high temperature. The model described herein is formulated in a way that is both physically insightful and experimentally accessible, grounded in random walk theory. As the understanding of heat transport is central to progress in energy science, this work guides engineering design principles in low thermal conductivity materials.

I. Introduction

The concept of a minimum thermal conductivity, κ_{min}, carried by the atomic vibrations of any solid material (crystalline or amorphous), is of practical technological importance. For example, materials screening and design for thermoelectric, thermal barrier and other thermal management applications often rely on models of κ_{min} to benchmark experimental observations or predict optimal material performance.[1–6] Due to the complexity of thermal conductivity there is not a unique definition of κ_{min}, and one practical option is to take relevant models of thermal conductivity and assume some limiting condition(s) that results in a reasonable estimate of what κ_{min} could be. It may also be argued that amorphous materials are systems where the experimentally measured κ would be closest to a predicted κ_{min}.

Most previous models of κ_{min} have largely relied on the phonon description of thermal conductivity (Fig. 1). The form of phonon mediated thermal conductivity (analogous to a kinetic gas) is

$$\kappa = \frac{1}{3}cv\ell, \quad (1)$$

where c is the heat capacity per unit volume, v is the average speed of a collective lattice vibration (phonon) and ℓ is the average phonon mean free path. The length scale of atomic disorder can be used to phenomenologically describe ℓ.[7,8] In the Kittel[8] and Clarke[4] models, the minimum thermal conductivity can be thought of as the limit $\ell \rightarrow a$ (a is the interatomic spacing). The Cahill[9,10] and Slack[11] models instead use a wavelength dependent mean free path to incorporate wave mechanics

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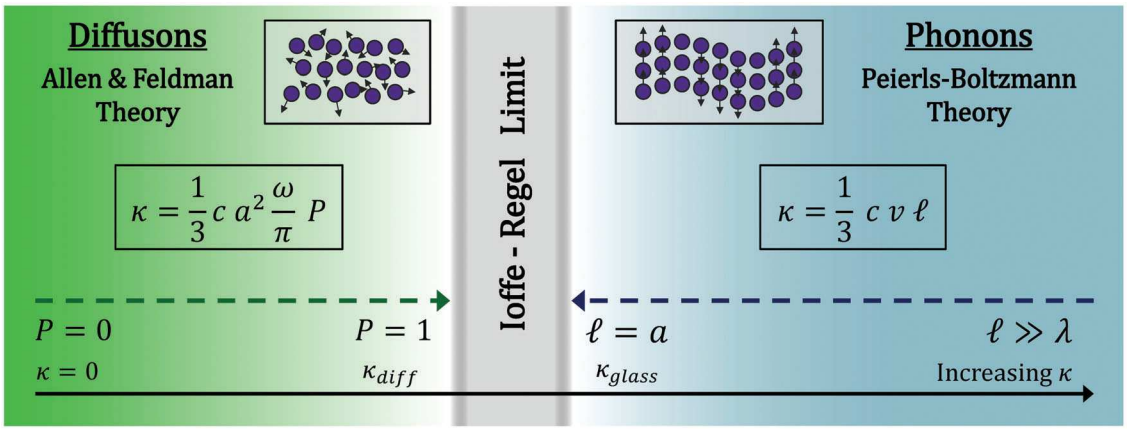

Fig. 1 Visual representation of the fundamental differences between phonon and diffuson models of thermal transport. The defining characteristics of phonon-based models include the speed of sound (v) and mean free path (ℓ). Diffuson-based models of Einstein,[20] formally defined by Allen and Feldman,[15–19] and that described here rely on a thermal diffusivity coming from random walk considerations, which leads to the jump attempt frequency ($2\omega/2\pi$) and the probability of a successful jump (P) being the operative theoretical inputs. Kittel ($\ell = a$),[8] Clarke ($\ell = a$),[4] Cahill ($\ell = \lambda/2$),[10] and Slack ($\ell = \lambda$)[11] made estimations of κ_{min} from a phonon perspective.

in the description of ℓ. Cahill uses $\ell = \lambda/2$, whereas Slack uses $\ell = \lambda$. These models work well for many materials and give an intuitive description of the phonon limit (at high temperature) of thermal conductivity (Fig. 1). However, as experimental thermal conductivities have been found below the Cahill and Clarke models, a different model/philosophy may provide insight into the limitations of phonon-based models and provide improved predictive power for experimentalists.

The mathematical description of lattice vibrations as phonons requires periodicity, which is not the case in amorphous materials or even nanomaterials and quasicrystals. Consequently, in the phonon picture of κ_{min} ($\ell \rightarrow a$, the so-called Ioffe–Regel limit[12] of phonons) the lattice vibration does not sample enough periodicity of the lattice to be a well-defined phonon or have the properties of such. Consequently, in this limit, it is technically more correct to define a diffusivity term, $\mathcal{D}$, which has the units of $v\ell$ ($m^2\ s^{-1}$) but v and ℓ are not independently defined, such that there is no need for a well-defined wavevector.[13] In the mechanism of diffusive thermal transport, heat is quantized by *diffusons*, characterized by a diffusivity. Diffusons can be present in any material, but may better describe atomic vibrations in materials with more atomic disorder (including crystals with large complex unit cells[14]).

Here we will use the diffuson theory of Allen and Feldman, thoroughly developed in ref. 15–19, to derive a phenomenological diffusive thermal conductivity, κ_{diff}, from the vibrational density of states. κ_{diff} is defined as the limit of entirely diffusive (diffuson mediated) thermal transport (Fig. 1). Even though the group velocity of phonons (measured by the speed of sound) is no longer the operative theoretical parameter, it can be incorporated *post hoc* by its correlation with the average frequency of the vibrational density of states. Lastly, by comparison of κ_{diff} with previous models of κ_{min} we suggest that κ_{diff} may be an appropriate estimation for κ_{min} in some cases. Whereby, κ_{diff} may help to explain materials with ultralow thermal conductivity.

II. Diffusive thermal conductivity

Any model for the thermal conductivity carried by the atomic vibrations of a solid must consider three components:

(i) the number of vibrations of a particular energy that are available to carry heat, *i.e.* the vibrational density of states, $g(\omega)$,

(ii) the quantity of heat that can be carried by each vibration, *i.e.* the heat capacity per mode, $C(\omega)$, and,

(iii) the propagation behavior of these vibrations through the material, *i.e.* the thermal diffusivity for each vibration, $\mathcal{D}(\omega)$.

Therefore, the total thermal conductivity can be written as the frequency-dependent integral

$$\kappa = \int_0^\infty g(\omega) C(\omega) \mathcal{D}(\omega) \mathrm{d}\omega. \quad (2)$$

The heat capacity, $C(\omega)$, for lattice vibrations follows from Bose–Einstein statistics:

$$C(\omega) = \frac{\partial}{\partial T}\left(\frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1}\right), \quad (3)$$

and saturates to $C(\omega) = k_B$ in the $T \rightarrow \infty$ limit. Consequently, the primary difference between thermal conductivity models is in the choice of physics used to characterize the propagation behavior, $\mathcal{D}(\omega)$.

The diffuson theory of Allen and Feldman explains diffusive thermal transport as the harmonic coupling between non-propagating (*i.e.*, not phonons or propagons), non-localized (*i.e.*, able to transfer energy, not locons) atomic vibrations. It is in the spirit of diffuson theory that we construct this phenomenological model. The propagation behavior of diffusons is derived assuming each diffuson travels according to the path of a random walk. In random walk theory, the net distance, x, traveled by a quantum after N discrete steps of size α is $x = \alpha\sqrt{N}$. This is related to the random walk diffusivity, $\mathcal{D}_{RW}$, and the elapsed time, t, through the parabolic relation

$$\mathcal{D}_{RW} = x^2/t = \alpha^2 N/t. \quad (4)$$

Here, N/t (number of steps per unit time) may be interpreted as the frequency of energy transfer attempts multiplied by the probability of a successful transfer, P. Einstein,[20] in his model for thermal conductivity (see also ref. 10), inferred that each oscillator made 2 attempts to transfer energy in one period of oscillation, $N/t = (2\omega/2\pi)P$. From eqn (4) we arrive at an isotropic approximation for the diffuson diffusivity,

$$\mathcal{D}_{\text{diff}}(\omega) = \frac{1}{3}\frac{n^{-\frac{2}{3}}\omega}{\pi}P, \tag{5}$$

by taking $\alpha = n^{-\frac{1}{3}}$ as the approximate jump distance between oscillators, where n is the number density of atoms. The factor of 1/3 comes from assuming a three dimensional system. Anisotropy may inhibit diffusion in certain directions and has ramifications discussed below. We also note that $P = 1$ is a theoretical maximum diffusivity for diffusons and is comparable to $\mathcal{D}_{\text{diff}}(\omega) = \frac{0.47}{3}n^{-\frac{2}{3}}\omega$ found by fitting N/t to MD results of the diffuson contribution to thermal transport in amorphous Si.[15] The other limit, $P = 0$, phenomenologically describes the condition for locons (*i.e.*, zero energy transfer). In the random walk diffuson picture, each oscillator acts completely independent from one another, resulting in a form of transport fundamentally different than that of phonons, where the phonon propagation is defined by a group velocity and relaxation time ($\mathcal{D} = \frac{1}{3}v_g{}^2\tau$).

Thus, eqn (2) can be composed from eqn (3) and (5) as the maximum (P = 1) diffusive thermal conductivity,

$$\kappa_{\text{diff}} = 3nk_{\text{B}}\int_0^\infty \left(\frac{g(\omega)}{3n}\right)\left(\frac{1}{3}\frac{n^{-\frac{2}{3}}\omega}{\pi}\right)\mathrm{d}\omega, \tag{6}$$

which simplifies to

$$\kappa_{\text{diff}} = \frac{n^{\frac{1}{3}}k_{\text{B}}\int_0^\infty g(\omega)\omega\,\mathrm{d}\omega}{\pi\int_0^\infty g(\omega)\,\mathrm{d}\omega} = \frac{n^{\frac{1}{3}}k_{\text{B}}}{\pi}\omega_{\text{avg}}. \tag{7}$$

Thus, it is the average oscillator frequency, ω_{avg}, which becomes the defining metric for the high temperature limit of diffuson-mediated thermal conductivity. In many cases ω_{avg} can be determined straightforwardly from inelastic neutron scattering experiments or computational methods. Furthermore, we will show that ω_{avg} may be approximated from speed of sound measurements and κ_{diff} may be appropriately used in the explanation of ultralow thermal conductivity materials.

By comparing eqn (5) and (6), it is possible to define the average diffuson diffusivity, $\bar{\mathcal{D}}_{\text{diff}}$, that is the weighted average of diffusivities, $\mathcal{D}_{\text{diff}}(\omega)$:

$$\bar{\mathcal{D}}_{\text{diff}} = \frac{\int_0^\infty g(\omega)\mathcal{D}_{\text{diff}}(\omega)\,\mathrm{d}\omega}{\int_0^\infty g(\omega)\,\mathrm{d}\omega} = \frac{n^{-\frac{2}{3}}\omega_{\text{avg}}}{3\pi}, \tag{8}$$

when P = 1.

Feldman, *et al.*[19] utilized molecular dynamics (MD) simulations to ascertain the spectral function $\mathcal{D}(\omega)$ for amorphous silicon. Thus, it is possible to compare the $\bar{\mathcal{D}}_{\text{diff}}$ calculated from eqn (8) with the average diffusivity value calculated from the MD results. Using the MD data shown in Fig. 2 of ref. 19, the average diffusivity of amorphous silicon was determined to be $\bar{\mathcal{D}}_{\text{MD}} = \frac{\int g(\omega)\mathcal{D}(\omega)\mathrm{d}\omega}{\int g(\omega)\mathrm{d}\omega} = 4.9\times10^{-3}$ cm^2 s^{-1}. The estimation using the average oscillator frequency ($\hbar\omega_{\text{avg}}$ = 44 meV[19]) and the number density of atoms for Si (Table 1) in eqn (8) gives

Table 1 Experimental number density of atoms ($n = \frac{\#\text{ atoms}}{\text{unit cell}}\times\frac{1}{V_{\text{uc}}}$) calculated from ICSD reported unit cell volumes (V_{uc}), and the longitudinal (v_{L}) and transverse (v_{T}) speeds of sound used to calculate the Debye temperature (θ_{D}) from the arithmetic average speed of sound, as well as the experimental average energy ($\hbar\omega_{\text{avg}}$) determined from the vibrational density of states

Element/compound	$n/10^{28}$ (# m^{-3})	v_{L} (m s^{-1})	v_{T} (m s^{-1})	Debye model $k_{\text{B}}\theta_{\text{D}}$ (meV)	Experimental $\hbar\omega_{\text{avg}}$ (meV)
RbI	2.03	2411[23]	1236[23]	11.39	7.69[24]
PbTe	2.67	3102[a]	1662[a]	16.42	7.85[25]
RbBr	2.46	2580[23]	1508[23]	13.92	9.16[24]
KI	2.30	2534[23]	1501[23]	13.47	9.71[24]
NaI	2.78	2716[23]	1688[23]	15.79	11.23[24]
KBr	2.69	3053[23]	1843[23]	17.26	11.52[24]
RbCl	2.81	3078[23]	2518[23]	21.09	11.99[24]
NaBr	3.70	3392[23]	2112[23]	21.71	13.70[24]
KCl	3.22	3896[23]	2366[23]	23.48	14.92[24]
$Cu_{2-\delta}Se$	6.02	3086[26]	1381[26]	19.60	16.20[27]
RbF	4.46	3946[23]	2333[23]	26.12	16.46[24]
NaCl	4.93	4470[28]	2570[28]	30.14	18.24[24]
KF	6.98	4608[23]	2842[23]	36.24	20.35[24]
NaF	8.03	5664[23]	3673[23]	48.00	27.89[24]
FeO	10.06	6630[29]	3230[29]	52.07	35.31[24]
CaO	7.17	8120[30]	4880[30]	63.51	37.78[24]
$SrTiO_3$	8.40	7860[31]	4680[31]	64.48	38.85[24]
Si	5.00	8480[32]	5860[32]	63.62	39.55[24]
ZnO	8.40	6000[23]	2831[23]	43.68	40.33[33]
MgO	10.69	9576[28]	6038[28]	87.88	49.75[24]
TiC	9.87	9429[34]	5856[34]	83.55	55.55[24]
SiC	9.64	11 730[28]	7430[28]	104.27	74.00[33]
c-BN	16.92	16 117[35]	10 653[35]	177.01	104.40[33]
Diamond	17.63	18 120[23]	12 323[23]	205.05	121.43[33]

[a] Measured by present authors (5 MHz pulse echo at 300 K)

$\bar{\mathcal{D}}_{\mathrm{diff}} = 5.2 \times 10^{-3}$ cm^2 s^{-1}. The agreement between the MD result and eqn (8) is quite good and provides some validation for the use of eqn (5). In fact, Allen and Feldman[15] use an equation with the same form as eqn (5) to fit their MD results in the context of diffuson-mediated thermal transport. They suggest that the agreement between the phenomenological model and the MD result supports the idea of a microscopic definition of minimum thermal conductivity.[15] Here, the random walk derivation of κ_{diff} allows for inferences about the physics of ultralow thermal conductivity, whereas ref. 14 and 15 are limited to dimensional analysis arguments.

However, it is important to note that the more-extensive MD study[19] indicates that there are both propagating (low energy, see arrow in Fig. 2 of ref. 19) and completely localized (high energy, see mobility edge line in Fig. 2 of ref. 19) vibrations in their model of amorphous Si, accounting for about 7% of the vibrational density of states.[17] Diffusons are proposed as the non-propagating, non-localized heat-carrying vibrations at intermediate energies. In the derivation of κ_{diff} (eqn (7)) from $\mathcal{D}_{\mathrm{diff}}(\omega)$ (eqn (5)), all vibrations contained within the density of states contribute to diffusive thermal transport, *i.e.* there are no propagating vibrations with larger contributions to thermal conductivity, and there are no localized vibrations that do not contribute to thermal conductivity. Consequently, κ_{diff} is the *diffuson*-mediated thermal conductivity. In using κ_{diff} as a type of κ_{min}, it should be recognized that experimental thermal conductivities found below κ_{diff} would tend to indicate that the material may have a significant number of localized vibrations (locons) that do not conduct heat; or, other exceptional physics may be at play, such as phonon focusing.[21]

III. Estimation of ω_{avg}

Although the derivation shows that it is possible to estimate κ_{diff} directly from $g(\omega)$, it is recognized that $g(\omega)$ is not always easily accessible experimentally or computationally, especially if the material system is complex (multi-phase, large unit cell, *etc.*). During the course of this study, it was found heuristically that the Debye temperature, θ_{D}, defined here by

$$k_{\mathrm{B}}\theta_{\mathrm{D}} = \hbar\omega_{\mathrm{D}} = \hbar(6\pi^2 n)^{1/3}\nu_{\mathrm{s}}, \tag{9}$$

can be used as a metric to estimate the experimentally determined ω_{avg}. It is important to recognize that, in the context of diffuson theory, θ_{D} may be regarded as a proxy for the influence of bond strength, atomic mass, and average atomic separation on the spectral distribution of the density of states. Specifically, by compiling $g(\omega)$, the arithmetic average speed of sound, $\nu_{\mathrm{s}} = \frac{1}{3}(2\nu_{\mathrm{T}} + \nu_{\mathrm{L}})$, and number density of atoms, n, for 24 compounds reported in the literature with speeds of sound spanning an order of magnitude (Table 1), we found the linear correlation (R^2 = 0.98) (Fig. 2)

$$\hbar\omega_{\mathrm{avg}} \approx 0.61 k_{\mathrm{B}}\theta_{\mathrm{D}}, \tag{10}$$

having a normalized root-mean-square error of 3.6% (RMSE ≈ 4 meV). It should be noted that the harmonic average speed of sound is another option for calculating the scalar θ_{D},[22] which was found to give a slightly worse correlation (R^2 = 0.97, RMSE ≈ 5 meV), but would still lead to the same conclusions drawn below. Other methods of estimating θ_{D} (*e.g.*, from low temperature heat capacity or inelastic neutron/X-ray scattering methods) are also expected to correlate with ω_{avg}.

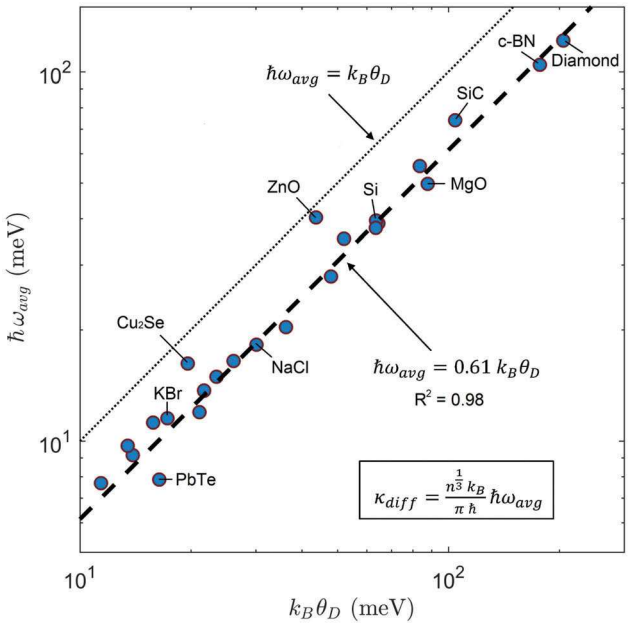

Fig. 2 A log–log plot demonstrating the linear correlation (eqn (10)) of the experimentally determined $\hbar\omega_{\mathrm{avg}}$ (found from the vibrational density of states) with the Debye temperature ($k_{\mathrm{B}}\theta_{\mathrm{D}} = \hbar(6\pi^2 n)^{1/3}\hbar\nu_{\mathrm{s}}$) calculated from the arithmetic average sound velocity ($\nu_{\mathrm{s}} = \frac{1}{3}(2\nu_{\mathrm{T}} + \nu_{\mathrm{L}})$) using the values found in Table 1. A linear slope of 1 is shown for reference (thin dotted line). Note that the Debye model would predict a linear slope of 0.75, which is substantially higher than this heuristic finding.

IV. Comparison of κ_{diff} with κ_{min} models

Next, we compare our diffuson thermal conductivity, κ_{diff}, to previous models of κ_{min} based on the maximum phonon scattering approach. This comparison gives good justification to use κ_{diff} as a new formulation of κ_{min}. Consequently, κ_{diff} may thus be used to explain the experimental results of ultralow thermal conductivity materials. First, we point out that eqn (10) can be used to further simplify eqn (7) to depend solely on n and ν_{s}:

$$\kappa_{\mathrm{diff}} \approx 0.76 n^{\frac{2}{3}} k_{\mathrm{B}} \frac{1}{3}(2\nu_{\mathrm{T}} + \nu_{\mathrm{L}}), \tag{11}$$

which makes this formulation of κ_{diff} directly comparable to the Cahill result,

$$\kappa_{\mathrm{glass}} = 1.21 n^{\frac{2}{3}} k_{\mathrm{B}} \frac{1}{3}(2\nu_{\mathrm{T}} + \nu_{\mathrm{L}}). \tag{12}$$

Here it is easily seen that κ_{diff} is approximately 37% lower than κ_{glass} on average. In fact, κ_{glass} is better used as a predictor for

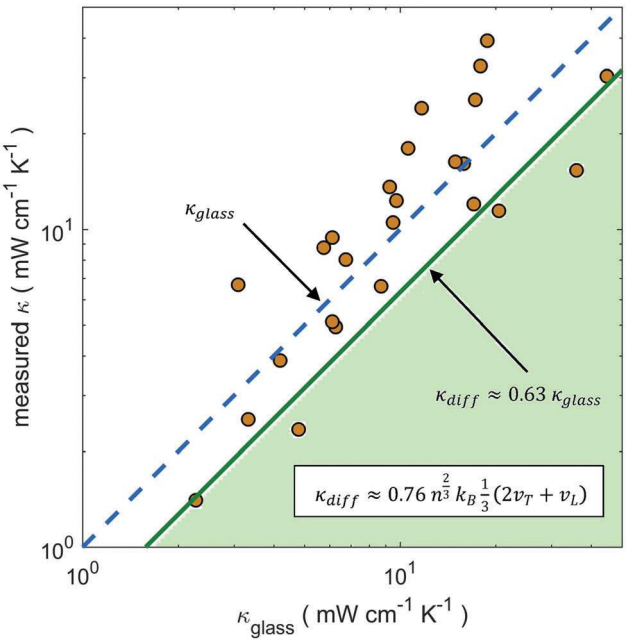

Fig. 3 A comparison of κ_{diff} with the Cahill model, κ_{glass}, shows that κ_{glass} is a good estimate for the measured thermal conductivity (within a factor of 2), whereas κ_{diff} may be a better metric for estimating the minimum thermal conductivity. Plotted points are the same that appear in Fig. 7 of ref. 36.

the experimental thermal conductivity of amorphous and disordered materials.[36] This is to say that, as a decent approximation, $\kappa_{glass} \approx \kappa_{measured}$ (within a factor of 2) and κ_{diff} may be a better estimation of κ_{min} (Fig. 3). The ideal κ_{min} would always predict a thermal conductivity that is lower than the measured value, and all of the data points in Fig. 3 would be to the left of that predicted line. Using κ_{diff} as κ_{min} very nearly satisfies this requirement, and only a few points remain to the right of the κ_{diff} line (shaded region in Fig. 3).

Further comparison shows that κ_{diff} is ≈18% lower than the κ_{min} equation presented by Clarke,[4]

$$\kappa_{\mathrm{min,Clarke}} = 0.87 n^{\frac{2}{3}} k_{\mathrm{B}} \sqrt{Y/\rho} \approx 0.93 n^{\frac{2}{3}} k_{\mathrm{B}} \frac{1}{3}(2v_{\mathrm{T}} + v_{\mathrm{L}}), \quad (13)$$

who also suggested that $\nu_s = \frac{1}{3}(2\nu_T + \nu_L) \approx 0.94\sqrt{Y/\rho}$ is a reasonable approximation (within 20%) for the speed of sound from Young's modulus, Y (N m^{-2}), and density, ρ (kg m^{-3}). As eqn (13) is effectively a restatement of the Kittel κ_{min}, these comparisons suggest that the diffuson mechanism of thermal transport conducts heat more slowly than the maximum phonon scattering limit predicts. This leads to the implication that materials with thermal conductivities near to κ_{diff} are transporting heat at a rate analogous to the maximum rate if all of the atomic vibrations were diffusons. Experimental thermal conductivities that fall below κ_{diff} would tend to indicate that there is some interesting/exceptional mechanism that is influencing thermal conductivity. Thus, κ_{diff} provides a reference value for the upper limit of diffusive thermal conductivity and may give some physical insight to conduction mechanisms in ultralow thermal conductivity materials.

V. Temperature dependent κ_{diff}

Although most thermoelectric generators, thermal barrier coatings and thermal management devices are concerned with temperatures at or above room temperature, making the high temperature limit of κ_{diff} the primary focus, it is important to make some remarks about the temperature dependence of the model presented above. The sole temperature dependence is incorporated through the heat capacity term, which accounts for the thermal activation of higher energy atomic vibrations as the temperature is raised from 0 K. Explicitly, eqn (3) can be rewritten as

$$C(\omega) = k_{\mathrm{B}} \left(\frac{\hbar\omega}{k_{\mathrm{B}}T}\right)^2 \frac{e^{\frac{\hbar\omega}{k_{\mathrm{B}}T}}}{\left(e^{\frac{\hbar\omega}{k_{\mathrm{B}}T}} - 1\right)^2} \quad (14)$$

which, in turn, can be used to incorporate a temperature dependence into eqn (6):

$$\kappa_{\mathrm{diff}}(T) = \frac{n^{\frac{1}{3}} k_{\mathrm{B}}}{\pi} \int_0^{\infty} \left(\frac{g(\omega)}{3n}\right) \left(\frac{\hbar\omega}{k_{\mathrm{B}}T}\right)^2 \frac{e^{\frac{\hbar\omega}{k_{\mathrm{B}}T}}}{\left(e^{\frac{\hbar\omega}{k_{\mathrm{B}}T}} - 1\right)^2} \omega \, \mathrm{d}\omega. \quad (15)$$

Here it is assumed that $g(\omega)$ and the diffusive mechanism of thermal transport are both reasonably independent of temperature. In effect, the integral in eqn (15) is a temperature dependent average frequency, $\omega_{avg}(T)$, of the vibrational spectrum,

$$\kappa_{\mathrm{diff}}(T) = \frac{n^{\frac{1}{3}} k_{\mathrm{B}}}{\pi} \omega_{\mathrm{avg}}(T), \quad (16)$$

and $\omega_{avg}(T)$ converges, of course, to a constant value (ω_{avg} in eqn (7)) when the entire vibrational spectrum is thermally activated in the $T \to \infty$ limit. However, it may be necessary to use $\kappa_{diff}(T)$ in the temperature range of interest if $T < \theta_{\mathrm{D}}$. This is to say that high energy vibrations that are not yet thermally activated should not be included in the calculation of κ_{diff}. Considering PbTe as an example, $g(\omega)$ is fairly independent of temperature up to 500 K.[25] The INS data at 100 K (Fig. 4A) was used for all calculations, and numerical integration of eqn (15) for temperatures up to 500 K reveals that $\kappa_{diff}(T)$ is converged to the high T value by 500 K (Fig. 4B). As the full vibrational spectrum (up to 16 meV in Fig. 4A) is excited by ≈190 K ($k_{\mathrm{B}}T \approx 16$ meV), the high temperature approximation is quite good for PbTe above room temperature.

The Einstein model of thermal conductivity, κ_{E} (see, *e.g.*, ref. 9), may be the most rudimentary equation for diffusive thermal transport, having a characteristic frequency, ω_{E}, that is constant with temperature and a density of states given by $g(\omega) = 3n\delta(\omega - \omega_{\mathrm{E}})$. Nevertheless, using $\omega_{\mathrm{E}} = \omega_{avg}$ (gray lines in Fig. 5) results in an Einstein model that converges to the value of κ_{diff} at high temperatures and goes as $\kappa_{\mathrm{E}} \propto e^{-\theta_{\mathrm{E}}/T}$ at low

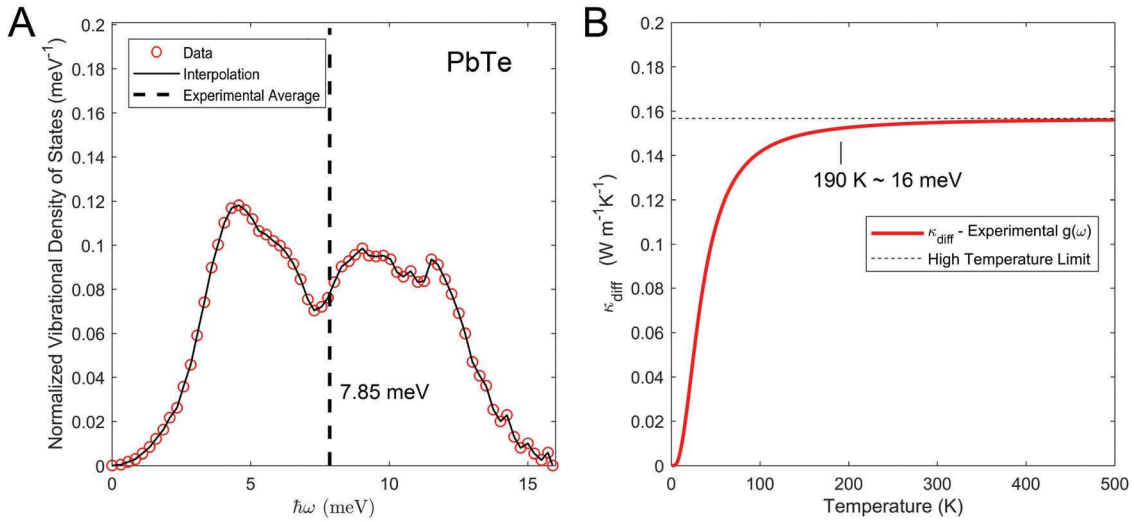

Fig. 4 The experimental vibrational density of states for PbTe at 100 K taken from ref. 25 (panel A) and the temperature dependent $\kappa_{diff}(T)$ calculated numerically using eqn (15), tending to κ_{diff} = 0.157 W m^{-1} K^{-1} at high temperature when the entire density of states is thermally excited (panel B).

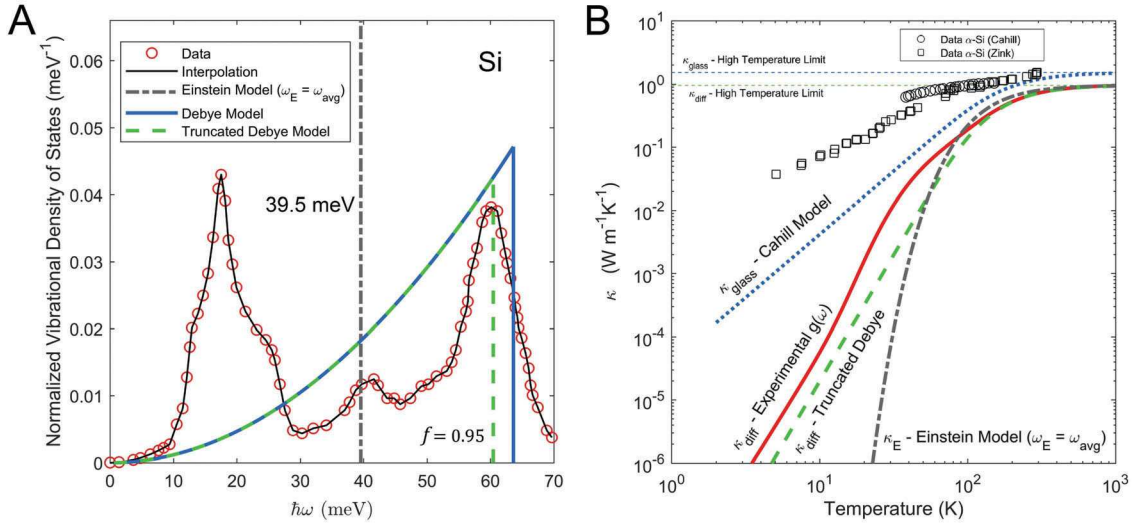

Fig. 5 The experimental vibrational density of states (red circles) for Si at 300 K taken from ref. 38, the Debye density of states (blue curve) having a maximum energy $k_B\theta_D$ determined by the speed of sound (Table 1), and the truncated Debye density of states (green curve) with a maximum energy $0.95k_B\theta_D$ (panel A). $\kappa_{diff}(T)$ was calculated numerically (κ_{diff} – experimental g(ω), red curve, using eqn (15)) and analytically (κ_{diff} – truncated Debye, green curve, using eqn (18)), and compared with the Cahill (κ_{glass}, blue curve) and Einstein (κ_E, gray curve) models, with experimental thermal conductivity measurements of amorphous Si[39,40] shown for reference (panel B). The low temperature behavior for each model is $\kappa_{diff} \propto T^4$, $\kappa_{glass} \propto T^2$, and $\kappa_E \propto e^{-\theta_E/T}$, respectively.

temperatures ($\theta_E = \hbar\omega_E/k_B$). As ω_E is the only and *ipso facto* the maximum frequency of the Einstein density of states, κ_E converges to the high temperature value of κ_{diff} at a lower temperature than if there were a distribution to the density of states (Fig. 5B). In order to better approximate the temperature dependence of κ_{diff} found numerically, it is possible to utilize the correlation between ω_{avg} and θ_D (eqn (10) and (11)), to estimate $\kappa_{diff}(T)$ using the Debye model $g(\omega) = \frac{3}{2\pi^2}\frac{\omega^2}{v_s^3}$ (blue curve in Fig. 5A). However, to converge at the high temperature value given by eqn (11), the upper limit of integration has to be changed to compensate for the fact that the average frequency of the Debye model is higher than that found experimentally. Explicitly,

$$\kappa_{diff} \approx \frac{n^{\frac{1}{3}}k_B}{\pi\hbar}(0.61k_B\theta_D) = k_B\int_0^{f\omega_D}\left(\frac{3}{2\pi^2}\frac{\omega^2}{v_s^3}\right)\left(\frac{n^{-\frac{2}{3}}\omega}{\pi}\right)d\omega \quad (17)$$

and equivalence with eqn (11) is achieved when the upper limit of integration is defined by $f \approx 0.95$ (truncated Debye model, green curve in Fig. 5A). Switching to the reduced variable,

$x = \hbar\omega/k_BT$, then $\kappa_{diff}(T)$ may be approximated as

$$\kappa_{diff}(T) \approx \frac{n^{-\frac{2}{3}}k_B}{2\pi^3 v_s^3}\left(\frac{k_BT}{\hbar}\right)^4 \int_0^{0.95\frac{\theta_D}{T}} \frac{x^5 e^x}{(e^x-1)^2}dx, \quad (18)$$

which predicts κ_{diff} goes as T^4 at low temperatures (Fig. 5B). This temperature dependence is a direct result of using a parabolic density of states (typical of propagating lattice waves) with a diffusivity of diffusons that is linear in ω. The Cahill model of κ_{glass} uses a parabolic density of states, but assumes phonon scattering is inversely proportional to ω, giving a diffusivity that is proportional to ω^{-1}. Thus, κ_{glass} goes as T^2 at low temperatures, in better agreement with the thermal conductivity of amorphous materials (Fig. 5B). Consequently, the thermal conductivity of real materials is likely dominated by propagating (phonon-like) vibrations at low temperatures, whereas κ_{min} at high temperature may be better described by diffuson-like vibrations. This conclusion is well-supported by a recent computational study on vibrations in a random $In_{1-x}Ga_xAs$ alloy.[37]

VI. Conclusion

The Kittel, Slack, and Cahill (phonon-based) models, *i.e.* κ_{glass}, are good approximations for amorphous materials particularly at low temperatures. However, at high temperature, thermal conductivities are sometimes even lower, suggesting that κ_{diff} may be a better estimate for a minimum thermal conductivity, κ_{min}. Here we define κ_{diff} as the limit of thermal conductivity when vibrations are not propagating (not phonon-like) but also not localized (specifically, $P = 1$).

Additionally, by correlating ω_{avg} with the Debye temperature ($\hbar\omega_{avg} \approx 0.61k_B\theta_D$) it is possible to estimate κ_{diff} from simple and accessible speed of sound measurements. From this correlation, we find that κ_{diff} is approximately 37% lower than the κ_{glass} estimate of Cahill using identical experimental inputs. In many cases, this may reconcile experimental observations with the concept of minimum thermal conductivity. However, observations of thermal conductivities below the κ_{diff} value are not unexpected, and would tend to indicate extraordinary physics leading to ultralow thermal conductivity. For example, complex materials may have a large number of localized (locon-like) vibrations that do not contribute to thermal conductivity; or, anisotropy may give rise to the exceptional mechanism of phonon focusing.

Finally, in the context of our analysis of PbTe, using κ_{diff} as a benchmark for minimum thermal conductivity leads to the conclusion that further reductions in thermal conductivity may be possible in many good thermoelectric materials.[41,42] Engineering the vibrational properties of these materials may lead to diffuson-like thermal transport, resulting in significant improvements to the thermoelectric figure of merit.

Author contributions

M. T. A. contributed to the compilation and analysis of the data. R. H. and G. J. S. contributed to data analysis and figure presentation. All authors participated in the writing and preparation of the manuscript.

Conflicts of interest

The authors declare that there are no conflicts of interest related to this work.

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