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Direct Solution to the Linearized Phonon Boltzmann Equation

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The frequency dependent phonon Boltzmann equation is transformed to an integral equation over the irreducible part of the Brillouin zone. Simultaneous diagonalization of the collision kernel of that equation and a symmetry crystal class operator allow us to obtain a spectral representation of the lattice thermal conductivity valid at finite frequency. Combining this approach with density functional calculations, an *ab initio* dynamical thermal conductivity is obtained for the first time. The static thermal conductivity is also obtained as a particular case. The method is applied to C, Si, and Mg_2Si and excellent agreement is obtained with the available static thermal conductivity measurements.

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The study of lattice heat transport in a crystal compound requires the knowledge of the phonon excitations as well as a model of transport which, in bulk systems, is conveniently taken to be the Boltzmann equation. Harmonic phonon spectra are routinely obtained from *ab initio* calculations based on the density functional theory, even for complicated compounds [1]. However to access transport properties like the thermal conductivity such calculations are not sufficient since it is necessary to describe the scattering of harmonic phonons by other phonons, impurities, and crystal boundaries. Among those three scattering processes the scattering by the others phonons is usually the more demanding since it originates in the anharmonic part of the total energy and therefore at least the third variation of the energy with respect to atomic displacements is needed. Such calculations, however, have been shown to be feasible, either from density perturbation theory [2], or using finite displacements [3].

Once these scattering processes are calculated, and the related collision matrices constructed, the transport Boltzmann equation still remains to be solved. Among the few published results for the *ab initio* calculations of the thermal conductivity, all solve this equation iteratively and consider the stationary case [4]. In the static case great progress has been made to reduce the number of iterations needed [5,6]. But it may still be desirable to have a complementary method, which allows us to access the dynamical lattice thermal conductivity. This can be of interest for applications. It is, for example, the case in thermoelectricity where the lattice thermal conductivity should be as small as possible to increase the figure of merit ZT. In this context the study of time- or frequency-dependent lattice thermal conductivity is also important and is the subject of intense research [7]. For a material to be a good thermoelectric it should have good electrical properties such that conductivity and thermopower but should also be a poor thermal conductor. These two requirements have proved to be difficult to be achieved together in bulk materials. One way to circumvent the difficulty is to nanostructurate the materials [8]. Another possibility may be to use finite frequency properties. It is known [9] that at a certain frequency the thermal conductivity starts dropping rapidly and that will increase the thermoelectric efficiency. The dropping frequency will be calculated here for the first time using *ab initio* calculations.

In this Letter I present a direct noniterative solution to the Boltzmann equation applicable to the stationary and nonstationary regime. This allows calculating the static and dynamical thermal conductivities and the accuracy of the method allows us to study materials which are good or poor thermal conductors. A single parameter controls the accuracy, mainly the number of points used to sample the first Brillouin zone. The Letter is organized as follows. The Boltzmann equation is first reduced to an integral equation over the irreducible part of the Brillouin zone. Then the thermal conductivity is expressed in terms of the collision operator defined during the reduction process. This operator is symmetric and, due to the reduction over the irreducible part of the Brillouin zone, is small enough to be diagonalized numerically. Consequently, a spectral representation is obtained for the thermal conductivity, valid at zero and finite frequency. Finally, the method is applied to compounds having from very large to very low thermal conductivity. In each case the agreement with experiment is excellent.

The phonon Boltzmann equation is an integral equation over the first Brillouin zone which in its linearized version takes the form [10]

$$\frac{\partial n^{(1)}_{qp}}{\partial t} + \frac{\partial n^{(0)}_{qp}}{\partial T}\frac{\partial T}{\partial \vec{r}} \cdot \vec{v}_{qp} = C(qp; n^{(1)}_{qp}) + \frac{1}{2}D(qp; n^{(1)}_{qp}). \tag{1}$$

The scattering of the phonon appears on the right-hand side of the equation through the term $C(qp)$ for the collision processes, and with $D(qp)$ for the decay processes. In the above equations n_{qp} is the occupation function for a phonon of wave vector q in branch p. $\vec{v}_{qp}$ is the velocity and $T = T(\vec{r}, t)$ the temperature. $n^{(0)}_{qp}$ is the occupation function at equilibrium, and $n^{(1)}_{qp}$ is the first order deviation from equilibrium, $n_{qp} \approx n^{(0)}_{qp} + n^{(1)}_{qp}$. It is possible to rearrange the scattering integral of Ref. [10] in order to make its relation to the lifetime of phonons calculated in [3] more explicit[11],

$$C(qp; n^{(1)}_{qp}) + \frac{1}{2} D(qp; n^{(1)}_{qp}) = -\sum_{q'p'} \Omega'_{qp,q'p'} n^{(1)}_{q'p'} \frac{\sinh(\frac{\hbar\omega_{q'p'}}{2k_BT})}{\sinh(\frac{\hbar\omega_{qp}}{2k_BT})} \tag{2}$$

with

$$\begin{aligned}\Omega'_{qp,q'p'} = {} & -\frac{\pi}{\hbar^2} \sum_{q_b p_b} |F^{pp'p_b}_{q-q'q_b}|^2 \frac{\Delta(q - q' + q_b)}{\sinh(\frac{\hbar\omega_{q_b p_b}}{2k_BT})} \\ & \times [\delta(\omega_{q'p'} - \omega_{qp} + \omega_{q_b p_b}) \\ & + \delta(\omega_{q'p'} - \omega_{qp} - \omega_{q_b p_b})] \\ & + \frac{\pi}{\hbar^2} \sum_{q_b p_b} |F^{pp'p_b}_{qq'q_b}|^2 \frac{\Delta(q + q' + q_b)}{\sinh(\frac{\hbar\omega_{q_b p_b}}{2k_BT})} \\ & \times \delta(\omega_{q'p'} + \omega_{qp} - \omega_{q_b p_b}) + \delta_{qq'} \delta_{pp'} \frac{1}{\tau_{qp}}.\end{aligned}$$

$F^{pp'p_b}_{qq'q_b}$ is the strength of the interaction in between the three phonons involved in the scattering [3] and Δ a function which is zero unless its argument is a reciprocal lattice vector, in which case it takes the value 1.

We can then make the following ansatz for $n^{(1)}_{qp}$, $\sinh(\hbar\omega_{qp}/2k_BT) n^{(1)}_{qp} \equiv f_{qp} \equiv \sum_{\alpha=1}^{3} \int dt' [\partial T(t')/\partial r_\alpha] \times f^{\alpha}_{qp}(t - t')$, where α is used to label the Cartesian components of the vector $\vec{f}_{qp}(t - t')$. If Eq. (1) is transformed to Fourier space we obtain

$$\begin{aligned} & -i\omega \vec{f}_{qp}(\omega) + \frac{\hbar\omega_{qp}}{4k_BT^2 \sinh(\frac{\hbar\omega_{qp}}{2k_BT})} \vec{v}_{qp} \\ & = -\sum_{q'p'} \Omega'_{qp,q'p'} \vec{f}_{q'p'}(\omega). \end{aligned} \tag{3}$$

The velocity is odd under inversion, $\vec{v}_{-qp} = -\vec{v}_{qp}$, and it is easy to check that the collision matrix is even, $\Omega'_{-qp,-q'p'} = \Omega'_{qp,q'p'}$, which means that $\vec{f}_{-qp}(\omega) = -\vec{f}_{qp}(\omega)$. Because the Brillouin zone contains q as well as $-q$ it shows that the collision matrix is not unique and that it is indeed possible to make other choices $\Omega_{qp,q'p'}$ such that $\sum_{q'p'} \Omega'_{qp,q'p'} \vec{f}_{qp}(\omega) = \sum_{q'p'} \Omega_{qp,q'p'} \vec{f}_{qp}(\omega)$. We choose to work with $\Omega_{qp,q'p'}$ given by

$$\begin{aligned}\Omega_{qp,q'p'} = {} & \delta_{qq'} \delta_{pp'} \frac{1}{\tau_{qp}} + \frac{\pi}{\hbar^2} \sum_{q_b p_b} |F^{pp'p_b}_{qq'q_b}|^2 \frac{\Delta(q + q' + q_b)}{\sinh(\frac{\hbar\omega_{q_b p_b}}{2k_BT})} \\ & \times [\delta(\omega_{q'p'} - \omega_{qp} + \omega_{q_b p_b}) \\ & + \delta(\omega_{q'p'} - \omega_{qp} - \omega_{q_b p_b}) \\ & + \delta(\omega_{q'p'} + \omega_{qp} - \omega_{q_b p_b})],\end{aligned}$$

which can be obtained by a dummy change of variable $q' \to -q'$ in the summation of Eq. (3). This matrix is clearly symmetric and can be shown to be positive definite using the same methods as [12].

In the following we denote by q a general point in the Brillouin zone, and by k a point in the irreducible part of the Brillouin zone. R are rotations of the isogonal point group g of the crystal and $|g|$ denotes the cardinal of that group. We denote by g_k the multiplicity for the branches of the star of k.

In Eq. (3) if we restrict the velocity field to the irreducible part of the Brillouin zone the Boltzmann equation becomes

$$\begin{aligned}\frac{\hbar\omega_{kp}}{4k_BT^2 \sinh(\frac{\hbar\omega_{kp}}{2k_BT})} v^{\alpha}_{kp} = {} & -\sum_{R'k'p'} (\Omega_{kp,R'k'p'} - i\omega \delta_{k,R'k'} \delta_{pp'}) \\ & \times \frac{g_{k'}}{|g|} f^{\alpha}_{R'k'p'}(\omega).\end{aligned}$$

Under the rotations R the velocity transforms like $v^{\alpha}_{Rkp} = \sum_{\beta} R_{\alpha\beta} v^{\beta}_{kp}$ and it can be checked that the collision matrix is invariant, $\Omega_{Rkp,Rk''p'} = \Omega_{kp,k'p'}$. Therefore, the Boltzmann equation written at point Rk shows that $f^{\alpha}_{R'k'p'}(\omega)$ and $\sum_{\beta} R^{-1}_{\alpha\beta} f^{\beta}_{RR'k'p'}(\omega)$ fulfills the same equation. This gives $f^{\alpha}_{Rkp}(\omega) = \sum_{\beta} R_{\alpha\beta} f^{\beta}_{kp}(\omega) + u^{\alpha}(\omega)$, where $\vec{u}(\omega)$ is any vector in the null space of $\Omega_{kp,R'k'p'} - i\omega \delta_{k,R'k'} \delta_{pp'}$. We will see later that the null space of this operator does not contribute to the lattice thermal conductivity and therefore that we can choose $\vec{u}(\omega) = 0$. In other words $\vec{f}_{kp}(\omega)$ transforms like the velocity and can therefore be understood as being proportional to the phonon mean free path. The Boltzmann equation can finally be reduced to an integral equation over the irreducible part of the Brillouin zone only,

$$\begin{aligned} & \frac{\hbar\omega_{kp}}{4k_BT^2 \sinh(\frac{\hbar\omega_{kp}}{2k_BT})} \sqrt{\frac{g_k}{|g|}} v^{\alpha}_{kp} \\ & = -\sum_{\beta k'p'} (\tilde{\Omega}_{\alpha kp,\beta k'p'} - i\omega \delta_{kk'} \delta_{pp'} P^{\alpha\beta}_{k'}) \sqrt{\frac{g_{k'}}{|g|}} f^{\beta}_{k'p'}(\omega)\end{aligned}$$

with

$$\tilde{\Omega}_{\alpha kp,\beta k'p'} = \sqrt{\frac{g_k g_{k'}}{|g|}} \sum_{R'} R'_{\alpha\beta} \Omega_{kp,R'k'p'} \quad \text{and}$$

$$P^{\alpha\beta}_{k} = \frac{g_k}{|g|} \sum_{R} R_{\alpha\beta} \delta_{k,Rk}.$$

In matrix notation this is written as $|X\rangle = -(\tilde{\Omega} - i\omega P)|f(\omega)\rangle$, with obvious definitions for $\tilde{\Omega}$ and P, and

$$|X\rangle_{\alpha kp} = \frac{\hbar\omega_{kp}}{4k_BT^2\sinh(\frac{\hbar\omega_{kp}}{2k_BT})}\sqrt{\frac{g_k}{|g|}}v^{\alpha}_{kp} \quad \text{and}$$

$$|f(\omega)\rangle_{\alpha kp} = \sqrt{\frac{g_k}{|g|}}f^{\alpha}_{kp}(\omega).$$

The operator P_k is working like the identity on vectors which transforms like the velocity, $P_k\vec{v}_{kp} = \vec{v}_{kp}$. $\tilde{\Omega}$ is a collision matrix. It shows that when working in the irreducible part of the Brillouin zone, and considering a transition from vector k to k', one should, obviously, also consider all the transitions to the different branches of the star of k'. Using the group properties of the set of rotation matrices, one can show that the matrices P_k and $\tilde{\Omega}$ are symmetric.

The energy flux through the lattice is given by $\vec{J}_E(t) = 1/V\sum_{qp}\hbar\omega_{qp}\vec{v}_{qp}n_{qp}(t)$; therefore, its Fourier transform is $\vec{J}_E(\omega) = -\kappa(\omega)\partial T/\partial\vec{r}(\omega)$ with the thermal conductivity tensor given by

$$\begin{aligned}\kappa^{\alpha\beta}(\omega) &= -\frac{1}{V}\sum_{qp}\frac{\hbar\omega_{qp}}{\sinh(\frac{\hbar\omega_{qp}}{2k_BT})}v^{\alpha}_{qp}f^{\beta}_{qp}(\omega)\\ &= \frac{4k_BT^2}{V}\sum_{qpq'p'}f^{\alpha}_{qp}(\omega)(\Omega_{qp,q'p'} - i\omega\delta_{q,q'}\delta_{pp'})\\ &\quad\times f^{\beta}_{q'p'}(\omega).\end{aligned}$$

In the second step we have shown that the factor of $f^{\beta}_{qp}(\omega)$ in the summand is just the drift term in the Boltzmann equation. As for the Boltzmann equation, the double integral over the Brillouin zone can be reduced to the irreducible part. We obtain

$$\kappa^{\alpha\beta}(\omega) = \frac{4k_BT^2}{V}\langle f(\omega)|\mathcal{I}(\alpha,\beta)(\tilde{\Omega} - i\omega P)|f(\omega)\rangle$$

with $\mathcal{I}_{\gamma kp,\gamma'k'p'}(\alpha,\beta) = \delta_{kk'}\delta_{pp'}\sum_R R_{\alpha\gamma}R_{\beta\gamma'}$. This operator is diagonal in the kp space. Its value for the Cartesian variables α and β depends on the symmetry class of the system and can easily be calculated using the great orthogonality theorem of groups theory. From its definition it is also clear that $\mathcal{I}(\alpha,\beta) = \mathcal{I}^t(\beta,\alpha)$ and that its purpose is to project out the components of the velocity and mean free path not involved it the $\alpha\beta$ component of the conductivity tensor. The operator $\tilde{\Omega}(\alpha,\beta;\omega) \equiv \mathcal{I}(\alpha,\beta)(\tilde{\Omega} - i\omega P)$ which appears in the thermal conductivity transforms the same way as $\mathcal{I}$, $\tilde{\Omega}(\alpha,\beta;\omega) = \tilde{\Omega}^t(\beta,\alpha;\omega)$; therefore, using the symmetry of $\tilde{\Omega}$ and P we obtain the commutation relation $[\mathcal{I}(\alpha,\beta), \tilde{\Omega} - i\omega P] = 0$. This last identity implies the Onsager reciprocity relations at finite frequency, $\kappa^{\alpha\beta}(\omega) = \kappa^{\beta\alpha}(\omega)$ and therefore allow us to obtain a more symmetric equation for the thermal conductivity,

$$\begin{aligned}\kappa^{\alpha\beta}(\omega) = \frac{2k_BT^2}{V}&\langle f(\omega)|[\mathcal{I}(\alpha,\beta) + \mathcal{I}(\beta,\alpha)]\\ &\times(\tilde{\Omega} - i\omega P)|f(\omega)\rangle,\end{aligned}$$

because $\mathcal{I}(\alpha,\beta) + \mathcal{I}(\beta,\alpha)$ is a symmetric matrix. It shows also that the null space of $[\mathcal{I}(\alpha,\beta) + \mathcal{I}(\beta,\alpha)](\tilde{\Omega} - i\omega P)$ does not contribute to the lattice thermal conductivity. A vector which belongs to the null space of $\tilde{\Omega} - i\omega P$ also belongs the null space of $[\mathcal{I}(\alpha,\beta) + \mathcal{I}(\beta,\alpha)](\tilde{\Omega} - i\omega P)$. Therefore, we can choose a solution to the Boltzmann equation which is orthogonal to $\ker(\tilde{\Omega} - i\omega P)$ and transforms like the velocities, $|f(\omega)\rangle = -(\tilde{\Omega} - i\omega P)^{\sim 1}|X\rangle$. Here ~ 1 is used to denote the Moore-Penrose inverse. The thermal conductivity can now be expressed as an average value over the known vector $|X\rangle$,

$$\kappa^{\alpha\beta}(\omega) = \frac{2k_BT^2}{V}\langle X|(\tilde{\Omega} - i\omega P)^{\sim 1}[\mathcal{I}(\alpha,\beta) + \mathcal{I}(\beta,\alpha)]|X\rangle.$$

The matrices $\mathcal{I}(\alpha,\beta) + \mathcal{I}(\beta,\alpha)$ and $\tilde{\Omega}$ are symmetric and commute. It is therefore possible to find a set of eigenvectors $|e_r\rangle$ such that $\tilde{\Omega}|e_r\rangle = \omega_r|e_r\rangle$ and $[\mathcal{I}(\alpha,\beta) + \mathcal{I}(\beta,\alpha)]|e_r\rangle = i_r(\alpha,\beta)|e_r\rangle$. This gives, finally, a spectral representation for the dynamical thermal conductivity,

$$\kappa^{\alpha\beta}(\omega) = \frac{2k_BT^2}{V}{\sum_r}'\frac{i_r(\alpha,\beta)|\langle X|e_r\rangle|^2}{\omega_r - i\omega} = \int d\omega'\frac{\rho_{\alpha\beta}(\omega')}{\omega' - i\omega}, \tag{4}$$

where $\rho_{\alpha\beta}(\omega')$ is a spectral density and the prime in the summation shows that the null space has to be excluded.

This method has been applied to materials with high (diamond), medium (silicon), and low (magnesium silicide) thermal conductivity. *Ab initio* calculations are performed to obtain the interaction strength in between the phonons, $F^{pp'p_b}_{qq'q_b}$, using the method in [3]. Therefore no adjustable parameters are used in the calculations. For the calculations of the thermal conductivity a 15 × 15 × 15 mesh is used to sample the Brillouin zone and the scattering by isotopes and surfaces have been included in the collision matrix. More details can be found in the Supplemental Material [13]. The results of the calculations are shown in Fig. 1(a) for the static thermal conductivity. In each case the agreement with experiment is excellent. This has to be related to the use of the previous equation which only involves the diagonalization of small matrices and where symmetry has been used at best to reduce numerical uncertainties.

The real (κ_r) and imaginary parts (κ_i) of the dynamical lattice thermal conductivity at room temperature are shown in Fig. 1(b) as a function of frequency. A rapid drop of κ_r is observed after some cutoff frequency $1/\tau_0$ which also correspond to a maximum in κ_i. Such a rapid decrease for κ_r has already been obtained in silicon using molecular dynamics calculations [14], and is known for long time [9],

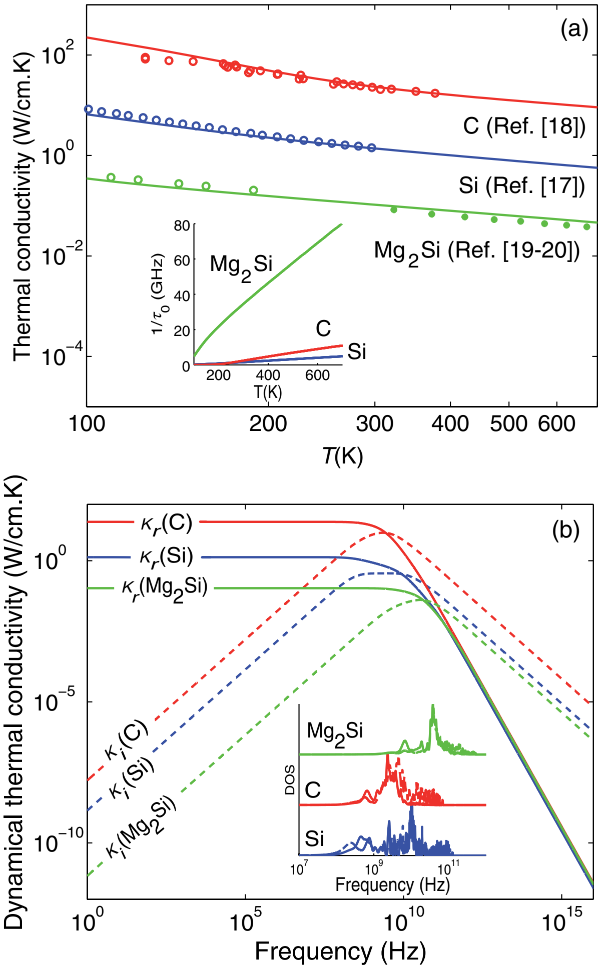

FIG. 1 (color online). Lattice thermal conductivities for diamond (red), Si (blue), and Mg_2Si (green). (a) The calculated (full lines) and experimental (circles) of static thermal conductivity as a function of temperature. Panel (b) shows the real (full lines) and imaginary (dashed lines) parts of the dynamical lattice thermal conductivity. The inset in panel (a) shows the inverse relaxation time τ_0 as a function of temperature. The inset in panel (b) shows spectral densities. The full line represents $\rho_{\alpha\beta}$, while for the dashed line it is just $\propto \sum_r \delta(\omega - \omega_r)$. The experimental data are taken from Refs. [17–20] as indicated in the figure.

in principle. When considering rapid time variation, the Fourier's law has to be modified to account for the finite time needed to establish current and thermal waves may eventually be formed. Notice that the calculated thermal conductivity is dependent upon the use of the linearized Boltzmann equation and as we have seen in Eq. (4), in some ways it characterizes it. From a physical point of view such a linearized equation, for example, through the use of an equilibrium distribution in the drift term, may not be sufficient when a rapid time variation is imposed on the system. The drift operator would need to be treated completely [15]. More generally, more work is needed for the calculation of the phonon second sound, but fortunately the structure of the equation to be considered does not change [16] and therefore our procedure can be applied. Such work is in progress.

The evolution of $1/\tau_0$ with temperature is shown in the inset of Fig. 1(a). It is clear that at high enough temperature it becomes proportional to the temperature, as required for a relaxation time. It can also be seen in Fig. 1(b) that the spread of κ_i looks broader for silicon. This may indicate that a single relaxation time is not sufficient to account for the dynamics and would lead to a more complicated evolution of the temperature. This is indeed confirmed by the spectral density $\rho_{\alpha\beta}$ plotted in the inset of Fig. 1(b) since there is a significant weight around 5×10^8 Hz.

To summarize, exploiting the symmetry of the system we have given a solution to the Boltzmann equation which allows us to compute the thermal conductivity from a spectral representation. It is done by computing the eigenvalues and eigenvectors of a symmetrized matrix of reduced dimensions. The numerical errors are therefore expected to be small. In addition it is no more difficult to obtain the dynamical thermal conductivity that is calculated here for the first time. This allows for a quantitative estimate of the drop frequency of κ_r. This can be of great interest in thermoelectric applications where κ needs to be reduced to increase ZT, but also for the industry of microprocessors. Considering their clock rate, heat transport at high frequency needs to be understood. The drop frequencies of the materials calculated here are very large but we should notice that the linearization of the Boltzmann equation may affect those values. Experimentally, a decrease of κ_r at much lower frequencies has been reported in alloy compounds [7] and could lead to applications elsewhere.

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