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Improved Callaway model for lattice thermal conductivity

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In developing the phonon quasiparticle picture, Peierls discovered that, in a perfect crystal, without anharmonic umklapp (U) events, a current-carrying distribution can never relax to a zero-current distribution. Callaway introduced a simplified approximate model version of the Peierls-Boltzmann equation, retaining its ability to deal separately with normal (N) and U events. This paper clarifies and improves the Callaway model, and shows that Callaway underestimated the suppression of N processes in relaxing thermal current. The new result should improve computations of thermal conductivity from relaxation-time studies.

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I. INTRODUCTION

Debye[1] was the first to realize that a perfect harmonic crystal is a perfect heat conductor. In insulators, heat is carried by propagating lattice-vibrational normal modes. Quantum theory simplifies by identifying these modes as particles. Anharmonic interactions permit a phonon with wave vector $\vec{Q}$ to interact with other phonons $\vec{Q}'$ and $\vec{Q}''$ (either by decay into two, or absorption of one and emission of the other). These events cause thermalization and resistance to current flow. The Peierls-Boltzmann equation[2] (PBE) puts this on a firm footing. Peierls made the important observation that wave-vector-conserving ("normal" or "N") events ($\vec{Q} = \vec{Q}' \pm \vec{Q}''$) can not by themselves cause a current-carrying state (with nonzero total wave vector) to decay to a zero current state, but that umklapp ("U") events ($\vec{Q} = \vec{Q}' \pm \vec{Q}'' + \vec{G}$, where $\vec{G}$ is a reciprocal lattice vector) can relax the current to zero.

Solving the PBE is still not an easy task, but modern advances make it possible. In particular, *ab initio* computation of harmonic normal modes is now very successful;[3] similar techniques give quite reliable anharmonic forces;[4] thus full solutions from purely theoretical input are now being done with good success.[5] This does not diminish the need for simplified approximate models to enable us to think about the physics of the process, and perhaps to invent reliable approximate treatments that avoid the full solution. Such a model was introduced by Callaway[6] in 1959. This model had a big influence on the field, although the model is rarely used in detail. Rethinking Callaway's model has allowed me to improve it, correcting and simplifying the solution. Then, using a Debye-type phonon model, the relative role of N and U processes is reanalyzed.

II. PEIERLS-BOLTZMANN EQUATION

The PBE is

$$\frac{dN_Q}{dt} = \frac{\partial N_Q}{\partial t} - \vec{v}_Q \cdot \frac{\partial N_Q}{\partial \vec{r}} + \left[\frac{\partial N_Q}{\partial t}\right]_{\text{collision}}, \qquad (1)$$

where Q is short for $(\vec{Q},n)$: both wave vector and the "branch indices" n needed to specify a propagating vibrational normal mode. The phonon group velocity is $\vec{v}_Q = \partial\omega_Q/\partial\vec{Q}$, where ω_Q is the frequency. The term "quasiparticle" denotes a propagating vibrational normal mode. Disorder and anharmonic interactions must not be so strong as to make the mean free path ℓ as short as a wavelength. The quasiparticle picture breaks down if the wave vector uncertainty caused by scattering is too large; ω_Q and $\vec{v}_Q$ are correspondingly poorly defined. If the heat-carrying excitations are not quasiparticles, then a theory more complicated than the PBE is needed. The Ioffe-Regel criterion,[7] which says no currents can flow if quasiparticles are destroyed ($\ell < \lambda$) is not correct. Better theories are sometimes available.[8,9] According to the PBE, the distribution N_Q may vary in space, and, if not driven, will relax under collisions to a local equilibrium Bose-Einstein distribution $n_Q[T(\vec{r})]$. The collision term is a complicated nonlinear sum over other phonon states $N_{Q'}$. The collisions conserve local energy

$$E = \sum_Q \hbar\omega_Q \left(N_Q(\vec{r}) + \frac{1}{2}\right). \qquad (2)$$

In the absence of anharmonic U events or other momentum-nonconserving processes (e.g., disorder), the total local wave vector

$$\vec{P}(\vec{r}) = \sum_Q \vec{Q} N_Q(\vec{r}) \qquad (3)$$

is also conserved under collisions.

The full Peierls-Boltzmann equation has an important property, namely, generating the Boltzmann "H-theorem".[10] As explained, e.g., by Landau and Lifshitz,[11] counting the multiplicity of states gives a quasiparticle entropy

$$S = k_B \sum_Q [(N_Q + 1)\ln(N_Q + 1) - N_Q \ln N_Q]. \qquad (4)$$

When this is maximized, subject to the constraint of constant E [Eq. (2)], the result is $N_Q \to n_Q$. Even though entropy is strictly not defined except in equilibrium, nevertheless, Eq. (4) qualifies as a nonequilibrium local quasiparticle entropy. When the PBE is used to compute the rate of change dS/dt of Eq. (4), one can show that $(dS/dt)_{\text{collision}} \geqslant 0$. The distribution N_Q that is stationary under collisions is the one that maximizes S under the relevant constraints. If the sole type of collision is anharmonic phonon scattering with only N processes, then the relevant object to maximize is

$$S/k_B - \beta E - \vec{\Lambda} \cdot \vec{P}, \qquad (5)$$

where β and $\vec{\Lambda}$ are Lagrange multipliers. The maximum occurs when N_Q evolves to a "flowing equilibrium" n^*_Q:

$$N_Q \to n^*_Q = [e^{\hbar\omega_Q/k_BT+\vec{\Lambda}\cdot\vec{Q}} - 1]^{-1}. \quad (6)$$

The Lagrange multiplier β has been identified as $1/k_BT$, with a local temperature $T(\vec{r})$, but the Lagrange multiplier $\vec{\Lambda}$ has still to be identified.

Now consider heat transport under an impressed temperature gradient. The steady state distribution obeys $dN_Q/dt = \partial N_Q/\partial t = 0$. The distribution function relaxes toward a local equilibrium (T may vary spatially), with a small deviation $N_Q \to n_Q + \Phi_Q$. The aim is to find, to first order in $\vec{\nabla}T$, the heat current, defined as

$$\vec{j} = (1/\Omega)\sum_Q \hbar\omega_Q \vec{v}_Q \Phi_Q \equiv -\kappa\cdot\vec{\nabla}T. \quad (7)$$

The spatial gradient term in the PBE [Eq. (1)] can be linearized in the thermal gradient; $\vec{v}_Q\cdot\vec{\nabla}N_Q$ becomes $(\partial n_Q/\partial T)\vec{v}_Q\cdot\vec{\nabla}T$. It is common to approximate the collision term by a simplified linear and local-in-Q approximation. The steady state, linear in $\vec{\nabla}T$, PBE, and the corresponding thermal conductivity become

$$0 \approx -\vec{v}_Q\cdot\vec{\nabla}T\ \partial n_Q/\partial T - \Phi_Q/\tau_Q, \quad (8)$$

$$\kappa_{\rm RTA} = \frac{1}{\Omega}\sum_Q \hbar\omega_Q v^2_{Qx}\tau_Q\ \partial n_Q/\partial T. \quad (9)$$

This is the relaxation-time approximation (RTA), and τ_Q is the phonon relaxation time. It is worth noting that, although this represents a serious approximation to the full PBE, nevertheless, the exact solution, if available, can always be put in the form of Eq. (9), with a suitably redefined relaxation time. The idea is that the exact distribution function $n_Q + \Phi_Q$, found by solving the linearized integral equation, can be written, in linear approximation, as $\Phi^{\rm exact}_Q \equiv -\tau^{\rm exact}_Q \vec{v}_Q\cdot\vec{\nabla}T\ \partial n_Q/\partial T$. This defines a quantity $\tau^{\rm exact}_Q$ which can be interpreted as the time for current relaxation in the channel Q. It is perhaps not very different from, but is surely not the same as, the ordinary "quasiparticle" relaxation time, defined using thermal Green's function theory via the self-energy (Σ), $1/\tau^{\rm QP}_Q \equiv -2\,{\rm Im}\Sigma({\rm Q},\omega+i\eta)$.

III. APPROXIMATE TREATMENT OF *N VERSUS U*

The question is how to find an approximate τ_Q that will give an accurate thermal conductivity, without the full labor of solving the PBE? The choice $\tau^{\rm QP}_Q$ has some advantages since it is a well-defined object, measurable by neutron or x-ray scattering, and not overwhelming to compute by modern methods. It is also an object of interest in Peierls-Boltzmann theory. If all phonons Q' are forced to be in equilibrium ($N_{Q'} = n_{Q'}$) except when Q' equals Q, then $(dN_Q/dt)_{\rm collision}$ becomes $-(N_Q - n_Q)/\tau^{\rm QP}_Q$. The PBE form for $\tau^{\rm QP}_Q$ agrees with the Green's function result in the usual anharmonic perturbation theory. The RTA consists of using $\tau^{\rm QP}_Q$ as the τ_Q in Eq. (8). This underestimates the thermal conductivity. When $N_Q \neq n_Q$, all collisions involving mode Q help relax the quasiparticle population of state Q; however, there are N processes which contribute to $\tau^{\rm QP}_Q$ but can not be fully active in relaxing the current. They do not fully contribute to $\tau^{\rm exact}_Q$. This is where the Callaway model[6] comes in.

Callaway's idea is to write $(\partial N_Q/\partial t)_{\rm collision}$ in two parts, as $-(N_Q - n_Q)/\tau^U_Q - (N_Q - n^*_Q)/\tau^N_Q$. The collective relaxation rate

$$1/\tau^c_Q = 1/\tau^U_Q + 1/\tau^N_Q \quad (10)$$

is just the total quasiparticle relaxation rate.[12] The part denoted $1/\tau^N_Q$, arising from anharmonic N processes, leaves the total crystal momentum unchanged. Only the "U" part $1/\tau^U_Q$ can relax to the final zero-current equilibrium. The part $1/\tau^N_Q$ relaxes the distribution to the flowing equilibrium n^*_Q [Eq. (6)]. When other mechanisms of phonon relaxation, such as disorder, are present, they also destroy crystal momentum conservation, and are grouped with the U terms.

The deviation $\Phi_Q = N_Q - n_Q$ [Eq. (7)] determines the current. Deviation from the flowing equilibrium can be written by Taylor expansion as $N_Q - n^*_Q = \Phi_Q + (k_BT^2/\hbar\omega_Q)(\partial n_Q/\partial T)\vec{\Lambda}\cdot\vec{Q}$. The Callaway-modified RTA therefore gives the distribution function as

$$\Phi_Q = -\tau^c_Q\vec{v}_Q\cdot\vec{\nabla}T\frac{\partial n_Q}{\partial T} - \frac{\tau^c_Q}{\tau^N_Q}\frac{k_BT^2}{\hbar\omega_Q}\vec{\Lambda}\cdot\vec{Q}\frac{\partial n_Q}{\partial T}. \quad (11)$$

The Lagrange multiplier $\vec{\Lambda}$ is not yet determined. This is where my answer deviates a bit from Callaway's.

The total crystal momentum $\vec{P}$ [Eq. (3)] should be the same for both the actual distribution N_Q and the flowing equilibrium distribution n^*_Q that N processes drive N_Q towards. This means

$$\sum_Q \vec{Q}(N_Q - n^*_Q) = 0 = \sum_Q \vec{Q}(\Phi_Q + n_Q - n^*_Q). \quad (12)$$

Taylor expanding gives

$$n_Q - n^*_Q = n_Q(n_Q+1)\vec{\Lambda}\cdot\vec{Q} = \frac{k_BT^2}{\hbar\omega_Q}\frac{\partial n_Q}{\partial T}\vec{\Lambda}\cdot\vec{Q}. \quad (13)$$

Inserting Eqs. (11) and (13) into Eq. (12) gives an equation for the Lagrange multiplier $\vec{\Lambda}$:

$$\sum_Q \tau^c_Q(\vec{v}_Q\cdot\vec{\nabla}T)\vec{Q}\frac{\partial n_Q}{\partial T} = \sum_Q \frac{\tau^c_Q}{\tau^U_Q}\frac{k_BT^2}{\hbar\omega_Q}(\vec{\Lambda}\cdot\vec{Q})\vec{Q}\frac{\partial n_Q}{\partial T}. \quad (14)$$

This replaces Eq. (14) of Callaway's paper,[6] which is equivalent except for an extra factor of $1/\tau^N_Q$ inside the sums on both sides of the equation. Why does Callaway have a different formula fixing $\vec{\Lambda}$? Callaway uses the constraint that the time rate of change of $\vec{P}$ from N processes must vanish. This is surely an equally exact statement, but, in order to implement it, Callaway makes an *additional* use of the relaxation time model. This gives an extra factor of $1/\tau^N_Q$ inside both Q sums in Eq. (12). The model is inexact, and leads to a difference from Eq. (14), which made no such additional approximation. Insofar as Callaway's Eq. (14) differs from Eq. (14), Callaway's method is wrong.

The argument simplifies by assuming cubic symmetry or else a thermal gradient along a symmetry axis (denoted x) of an orthorhombic crystal. Then only Λ_x is needed. Its value

cancels from Eq. (11) when the second term is multiplied by the left-hand side, and divided by the right-hand side, of Eq. (14). When the resulting equation for Φ_Q is substituted into Eq. (7), a formula for the thermal conductivity results:

$$\kappa_{xx} = \kappa_c + \lambda_1\lambda_2/\lambda_3. \tag{15}$$

The leading term κ_c is just the usual relaxation time formula

$$\kappa_c = \frac{1}{\Omega}\sum_Q \hbar\omega_Q v_{Qx}^2 \tau_Q^c \, \partial n_Q/\partial T, \tag{16}$$

where $1/\tau_Q^c$ is the usual quasiparticle relaxation rate $1/\tau_Q^U + 1/\tau_Q^N$ containing both N and U processes. The correction factors are

$$\lambda_1 = \frac{1}{\Omega}\sum_Q v_{Qx} Q_x \tau_Q^c \, \partial n_Q/\partial T, \tag{17}$$

$$\lambda_2 = \frac{1}{\Omega}\sum_Q v_{Qx} Q_x \left(\tau_Q^c/\tau_Q^N\right)\partial n_Q/\partial T, \tag{18}$$

$$\lambda_3 = \frac{1}{\Omega}\sum_Q \left(Q_x^2/\hbar\omega_Q\right)\left(\tau_Q^c/\tau_Q^U\right)\partial n_Q/\partial T. \tag{19}$$

Equations (15)–(19) are the new result of this paper. They are an approximate procedure, based on the Callaway model, which better contains the different roles of N and U scattering events. Callaway's answer is similar, except that τ_Q^c is replaced by the ratio τ_Q^c/τ_Q^N in both λ_1 [Eq. (17)] and λ_3 [Eq. (19)].

To see the consequence of this modification, the Debye model is appropriate. It assumes three branches $\omega_Q = vQ$, with v a constant sound velocity, the same for simplicity, for all three branches. The dispersion relations are spherically symmetric, and the Brillouin zone approximated by a sphere of radius Q_D with maximum frequency $\omega_D = vQ_D$. The Debye density of states is $\mathcal{D}(\omega) = (9N/V)\omega^2/\omega_D^3$. The specific heat is

$$C(T) = \int_0^{\omega_D} d\omega \hbar\omega \frac{\partial n(\omega)}{\partial T}\mathcal{D}(\omega). \tag{20}$$

In the same spirit, one assumes scattering rates $1/\tau_Q^N$ and $1/\tau_Q^U$ to depend only on ω_Q and T, that is, the only Q dependence comes through ω_Q. Furthermore, it is common to assume that the resulting function factorizes into a power of frequency ω times a function of T:

$$1/\tau_Q^\alpha \to 1/\tau_\alpha(\omega_Q, T) = \gamma_\alpha(T) \times (\omega_Q/\omega_D)^{p_\alpha}. \tag{21}$$

If we look only at ratios, it will not be necessary to choose a T dependence of γ_N. For γ_U's, at low T, the needed large Q thermal phonon is thermally suppressed by a factor often written as $\gamma_U = \gamma_N \times A\exp(-\Theta_D/aT)$, where A is a constant, independent of T, and Θ_D is the Debye temperature $k_B\Theta_D = \hbar\omega_D$. The adjustable parameter a is often set to 3.

It is convenient to define a frequency average $\overline{f}$ of a frequency-dependent function $f(\omega)$ as

$$\overline{f}(T) = \frac{1}{C(T)}\int_0^{\omega_D} d\omega \hbar\omega \frac{\partial n(\omega)}{\partial T}\mathcal{D}(\omega) f(\omega). \tag{22}$$

Then in the Debye model, the answers (16)–(19) become

$$\begin{aligned}
\kappa_{cD} &= \frac{1}{3}C(T)v^2\overline{\tau_c}, \\
\lambda_{1D} &= \frac{1}{3\hbar}C(T)\overline{\tau_c}, \\
\lambda_{2D} &= \frac{1}{3\hbar}C(T)\overline{\tau_c/\tau_N}, \\
\lambda_{3D} &= \frac{1}{3\hbar^2 v^2}C(T)\overline{\tau_c/\tau_U}.
\end{aligned} \tag{23}$$

Then my result for the Callaway model in Debye approximation is

$$\kappa_C = \kappa_{\rm RTA}\left(1 + \frac{\overline{\tau_c(\omega,T)/\tau_N(\omega,T)}}{\overline{\tau_c(\omega,T)/\tau_U(\omega,T)}}\right). \tag{24}$$

Callaway's solution has an extra factor $1/\tau_Q^N$ in both λ_1 and λ_3. Then Eq. (24) is replaced by

$$\kappa_C^* = \kappa_{\rm RTA}\left(1 + \frac{\overline{\tau_c(\omega,T)/\tau_N(\omega,T)}^2}{\overline{\tau_c(\omega,T)}\;\overline{\tau_c(\omega,T)/\tau_U(\omega,T)\tau_N(\omega,T)}}\right). \tag{25}$$

The notations κ_C and κ_C^* denote the present (new and corrected) solution of Callaway's model in Debye approximation, and the original (old and uncorrected) solution.

Finally, it is necessary to choose power laws p_N and p_U for N and U scattering rates. Following Herring,[13] the N processes are assumed to have quadratic ω dependence $p_N = 2$. This has been confirmed in recent numerical calculations.[14,15] Herring also suggested quadratic behavior $p_U = 2$ for the ω dependence of U processes. However, numerical calculations have been recently fit to larger powers $p_U = 4$ (Ref. 14) and $p_U = 3$ (Ref. 15). Results for two cases $p_U = 2$ (Herring) and $p_U = 4$ (a possible alternative) are shown in Fig. 1.

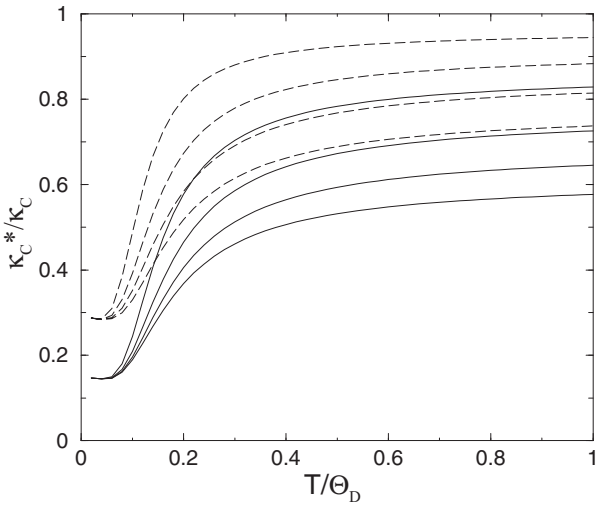

FIG. 1. Ratio of Callaway's old solution (κ_C^*) to the new solution (κ_C) of the Callaway model in Debye approximation, with quadratic behavior $1/\tau_N(\omega) = \gamma_N(\omega/\omega_D)^2$. The dashed curves use the Herring quadratic behavior also for U, with ratio $\tau_N(\omega)/\tau_U(\omega) = \gamma_U/\gamma_N = g$ and $g = A\exp(-\Theta_D/3T)$. The solid curves have $p_U = 4$ or $\tau_N(\omega)/\tau_U(\omega) = g(\omega/\omega_D)^2$, and the same form for g. In both cases, the four curves, from lowest to highest, are for values of A set to 1, 2, 4, and 10.

Callaway's solution κ_C^* underestimates the suppression of N scattering, and thus underestimates the thermal conductivity. I believe that κ_C, the larger solution, is the true solution of Callaway's model. In the low-T limit, integrals can be done analytically. In Herring's case ($p_N = p_U = 2$), the ratio $\kappa_C^*/\kappa_C \to 7/25$, and in the case $p_N = 2$, $p_U = 4$, the ratio becomes $\kappa_C^*/\kappa_C \to 1/7$. At higher T, as U scattering increases to the level of N scattering, the difference between Callaway's old solution and the present new one is smaller.

The new solution simplifies in the case $p_N = p_U$ as, for example, in Herring's case where both are 2. The complexities in Eq. (24) cancel, leaving $\kappa_C \to \kappa_{\rm RTA} \times (1 + \gamma_N/\gamma_U)$. This is true at all T, leaving the simple answer $\kappa_C = (1/3)Cv^2\overline{\tau_U(T,\omega)}$; N scattering drops out completely. This is definitely not true of Callaway's solution. For more realistic models, for example, with $p_U = 4$, frequency integrals are more complicated, and N scattering does not completely disappear. In fact, since U scattering has apparently an ω^3 or ω^4 limiting behavior, and impurity scattering has the Rayleigh form $\gamma_{\rm imp} \propto \omega^4$, the quadratic behavior of the N term is the only thing that prevents a low-ω divergence in the integrals. A low-ω divergence is not completely unphysical. At low enough T, the only vibrations thermally excited are sure to have mean free paths longer than sample size. Whether or not their contribution to the integrals for κ converge, they in fact do not contribute currents governed by temperature gradients. Instead, they give ballistic currents determined by the difference available heat (i.e., T^4) in the baths at the two ends. The integrals have to be cut off at some $\omega_{\rm min}$ whose value depends on sample size.

Figure 2 shows some of the same results as Fig. 1, except in a different ratio, comparing with the relaxation-time approximation rather than the original Callaway approximation. Also shown is the effect of including large amounts of momentum-nonconserving impurity scattering. Enhancement of thermal conductivity is still quite large since N scattering dominates $1/\tau_{\rm QP}$ at low T. However, the enhancement is smaller because $1/\tau_{\rm imp}$ exceeds $1/\tau_U$ at lower T.

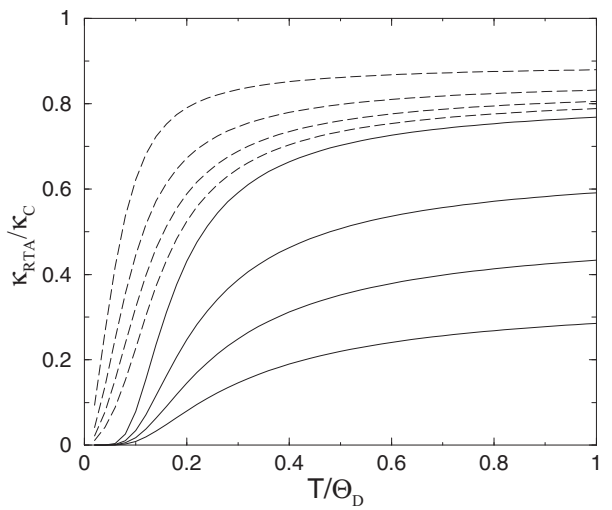

FIG. 2. Ratio of relaxation-time approximation ($\kappa_{\rm RTA}$) to full solution κ_C for the Callaway model in Debye approximation with quadratic ω dependence for $1/\tau_N$ and quartic ω dependence for $1/\tau_U$. The four solid curves use the same parameters as the solid curves of Fig. 1. The dashed curves have $A = 10$ (as does the top solid curve), but also include Rayleigh-type impurity scattering [$1/\tau_{\rm imp} = \gamma_{\rm imp}(\omega/\omega_D)^4$], a momentum-nonconserving event which adds to $1/\tau_U$ without the low-T thermal suppression. The strength of the impurity term is $\gamma_{\rm imp}/\gamma_N = 1, 2, 4, 10$ (from the lowest dashed curve to the highest).

IV. CALLAWAY'S MODEL AND REALITY

Computation is now advanced enough to give a final answer to the question: How realistic is Callaway's model? There are good algorithms for accurate construction and solution of the PBE, at least at T not too low (where mesh size becomes a problem because only small $\vec{Q}$ phonons are excited.) An iterative solution of the PBE begins with a first iteration which is the RTA. This requires full computation of the quasiparticle relaxation rate $1/\tau_Q^{\rm QP}$. It is straightforward in principle to separate this into N and U parts. These could be used to obtain the Callaway model solution from λ_1, λ_2, and λ_3 of Eqs. (17)–(19). If a full interative solution of the PBE is then completed, it would be interesting to compare with the Callaway solution.

In the Herring version of the Debye approximation to the Callaway model, with anharmonic phonon scattering rates going like $1/\tau_Q \propto \omega_Q^2$ for both N and U, the answer is that N processes drop out, and the umklapp scattering determines the conductivity. This is a nice but oversimple result. Once the model gets more complex, with multiple momentum relaxing processes with differing ω dependencies, N processes no longer drop out completely, but can not alone relax the distribution N_Q to the zero-current distribution. For models more realistic than Debye, N processes can relax the current toward a value $\hbar\langle v^2\rangle\vec{P}/\Omega$, but still can not relax the current completely.

There has been a practice of computing only $\kappa_{\rm RTA}$, sometimes with the claim that the Boltzmann equation has thus been solved. Two arguments may seem to support this. First, Callaway used his solution to fit quite accurately the measured $\kappa(T)$ of Ge. He did not find much enhancement beyond RTA from the reduced role of N processes. This must be, at least partly, an artifact of the inaccuracy of his solution. Thus, Callaway's work seems to approximately support the RTA, but the support can not be taken seriously. The second argument is that the corrections are not often as big in complex materials as they are in the Debye model shown in Figs. 1 and 2.

Several converged iterative solutions of the PBE have been reported that include some discussion of the departure of the full solution from the RTA. Ward *et al.*[16] in Fig. 2 show an 80% increase in κ(172 K) for diamond, by converging the PBE rather than using RTA. The increase lowers to 30% at 1200 K. However, in other systems, the error is often not so large. For example, Fig. 3 of Chernatynskiy *et al.*[17] shows that for MgO, the effect on $\kappa(T = 300\ {\rm K})$ is only a 7% increase, and the effect is smaller in UO_2. In $SrTiO_3$, where the effect is tiny at 250 K, it is 7% at 50 K and a 42% increase at 20 K.[18] The message is that for materials with complex phonon spectra, U processes are only thermally suppressed at quite low T. This is why the inability of N processes alone to degrade

heat current does not show up except at low T and with pure samples (including isotopic purity). The recent prediction of large κ in BAs (Ref. 19) is related to weakness of U processes (and the resulting ineffectiveness of N processes) caused by phonon dispersion that is quite simple and also unusual. It would be interesting to ask whether the Callaway model has decent predictive power in this case. Even if not predictive, the Callaway model has given needed insight, and should continue to do so. Therefore, the corrected (and simpler) solution of this model found in this paper should have some value.

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[1] P. Debye, in *Lectures on the Kinetic Theory of Matter and Electricity*, edited by M. Planck (Teubner, Leipzig, 1914), pp. 19–60.

[2] R. Peierls, Ann. Phys. (NY) **3**, 1055 (1929).

[3] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001).

[4] X. Gonze and J.-P. Vigneron, Phys. Rev. B **39**, 13120 (1989); A. Debernardi, S. Baroni, and E. Molinari, Phys. Rev. Lett. **75**, 1819 (1995); G. Lang, K. Karch, M. Schmitt, P. Pavone, A. P. Mayer, R. K. Wehner, and D. Strauch, Phys. Rev. B **59**, 6182 (1999).

[5] D. A. Broido, M. Malorny, G. Birner, N. Mingo, and D. A. Stewart, Appl. Phys. Lett. **91**, 231922 (2007).

[6] J. Callaway, Phys. Rev. **113**, 1046 (1959).

[7] A. F. Ioffe and A. R. Regel, in *Progress in Semiconductors*, edited by A. F. Gibson (Wiley, New York, 1960), Vol. 4, pp. 237–391.

[8] Y. M. Beltukov, V. I. Kozub, and D. A. Parshin, Phys. Rev. B **87**, 134203 (2013).

[9] P. B. Allen and J. L. Feldman, Phys. Rev. Lett. **62**, 645 (1989); Phys. Rev. B **48**, 12581 (1993).

[10] W. Pauli, in *Festschrift zum 60. Geburtstage A. Sommerfeld*, edited by P. Debye (Hirzel, Leipzig, 1928), p. 30.

[11] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 3rd ed. (Pergamon, Oxford, 1980), p. 160.

[12] The best choice is presumed to be when $1/\tau_Q^c = 1/\tau_Q^{\rm QP}$. Callaway's notation $1/\tau_Q^c$ allows other models, presumably less accurate.

[13] C. Herring, Phys. Rev. **95**, 954 (1954).

[14] A. Ward and D. A. Broido, Phys. Rev. B **81**, 085205 (2010).

[15] K. Esfarjani, G. Chen, and H. T. Stokes, Phys. Rev. B **84**, 085204 (2011).

[16] A. Ward, D. A. Broido, D. A. Stewart, and G. Deinzer, Phys. Rev. B **80**, 125203 (2009).

[17] A. Chernatynskiy, J. E. Turney, A. J. H. McGaughey, C. H. Amon, and S. R. Phillpot, J. Am. Ceram. Soc. **94**, 3523 (2011).

[18] A. Chernatynskiy (private communication).

[19] L. Lindsay, D. A. Broido, and T. L. Reinecke, Phys. Rev. Lett. **111**, 025901 (2013).