Improved Variational Principles for Transport Coefficients*

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A sequence of variational principles for converting a trial solution of a linearized Boltzmann equation into bounds on a transport coefficient is presented. For systems in which the Boltzmann collision operator has a bounded eigenvalue spectrum, we obtain an infinite sequence of lower bounds which begins with the familiar result of Ziman. For an arbitrary trial function, this sequence converges monotonically to the exact transport coefficient. Application of the first two terms has been made to the lattice thermal conductivity of a model simulating solid argon; the second bound lies considerably higher than the first.

I. INTRODUCTION

MOST theoretical study of transport coefficients in recent years has been from one of three approaches. On the formal side, numerous authors have used the Kubo formalism to relate the linear response of a system to a disturbance ultimately to some quasiparticle Green's function. Some of these authors intentionally avoid the question of describing the transport process by a kinetic equation; others derive such an equation. On the practical side, the solutions to relaxation-time forms of quasiparticle Boltzmann equations have been used to analyze a great body of experimental data. This approach very conveniently gives information about the relative importance of different attenuation mechanisms, but the theory is a phenomenological one, whose parameters are difficult to interpret at a fundamental level.

Somewhere between these two approaches lie the techniques for bounding transport coefficients, originally developed by Kohler,[1] Sondheimer,[2] Leibfried and Schlömann,[3,4] and Ziman.[5] Here too, one presupposes a Boltzmann-like transport equation for the space-and-time-dependent occupation number $N_q(\mathbf{r},t)$ of a single quasiparticle state specified by indices q (e.g., wave vector and polarization, for phonons). One then seeks to discover or invent a functional $\mathcal{K}(N_q)$ which has a stationary point at the distribution N_q satisfying the transport equation, and whose stationary value is the desired transport coefficient. By evaluating $\mathcal{K}$ for a distribution only approximately satisfying the transport equation, one then obtains an upper or lower bound on the transport coefficient. This approach provides a controlled means of approximating transport coefficients, without mutilation of the collision operator in the transport equation, and is suitable for computation.

Recently, Jensen, Smith, and Wilkins[6] have studied several functionals other than the standard one (as discussed for instance by Ziman[5]), and have used them to bound transport coefficients in a degenerate Fermi liquid. Unfortunately, in several other physically interesting systems the complexity of the quasiparticle collision operator precludes direct application of these new ideas; a system of interacting phonons is one such case. Nevertheless, the method of Jensen, Smith, and Wilkins suggests a new approach to bounding transport coefficients, which is presented in this report.

The approach is not general. The new bounds we derive are useful only when the linearized collision operator for the system under study possesses a bounded spectrum of eigenvalues. For the case of interacting phonons, we shall show this property to be a rather general feature of anharmonic interactions. It is also known that the property holds for a classical gas with a soft interaction potential.[7] Under the rather formal condition that the regular part of the collision operator is completely continuous[8] (which as far as we know has been verified only for the classical Boltzmann equation[7]), boundedness of the total spectrum is implied by boundedness of the spectrum of quasiparticle relaxation rates—the diagonal elements of the collision operator in a representation based on quasiparticle eigenstates. Since no quasiparticle should have a relaxation rate larger than its own excitation frequency, one is tempted to guess that the above boundedness property of the collision operator's spectrum holds for any system in which the *energy* spectrum of noninteracting quasiparticles is bounded. This would include electron-electron and electron-phonon systems in solids, so long as only a finite number of one-electron bands need be considered. The guess, of course, presupposes the unverified complete-continuity condition.

For collision operators with a bounded spectrum, we find an infinite sequence of functions $\mathcal{K}_m<(N_q)$,

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[4] G. Leibfried, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 7/1, p. 104.

[5] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1960), Chaps. 7 and 8.

[6] H. H. Jensen, H. Smith, and J. W. Wilkins, Phys. Rev. **185**, 323 (1969).

[7] H. Grad, *Rarefied Gas Dynamics*, edited by J. A. Laurmann (Academic Press Inc., New York, 1963), Vol. II, p. 26.

[8] F. Riesz and B. Sz.-Nagy, *Functional Analysis* (Frederick Ungar Publishing Co., New York, 1955), Chaps. 4 and 6, Sec. 134.

$m=0, 1, 2, \ldots$, all of which bound the transport coefficient from below. The beginning term $\mathcal{K}_0^<$ yields the lower bound of Ziman. For an *arbitrary* trial function N_q, the sequence converges monotonically to the exact transport coefficient. This sequence of bounds is presented in a general fashion in Sec. II. The remainder of the paper is devoted to the details of applying the bounds to calculations of lattice thermal conductivity. The proof that the phonon collision operator has a bounded eigenvalue spectrum is given in Sec. IV and the Appendix. For a simplified lattice model, we have evaluated $\mathcal{K}_0^<$ and $\mathcal{K}_1^<$, and find a considerable difference between them.

II. SEQUENCE OF BOUNDS

We wish to discuss an inhomogeneous linear equation of the form

$$\chi_q=\sum_{q'} H_{qq'}v_{q'}. \tag{1}$$

Here χ_q is the known real inhomogeneous term and the $H_{qq'}$ are given elements of a real, symmetric, positive definite or positive semidefinite linear operator with a bounded spectrum of eigenvalues h_i, $0\leq h_i\leq h_{\max}$.

A steady-state linearized Boltzmann equation can be cast in this form, with all properties but that of the boundedness of the spectrum of the collision operator H following from detailed balance and macroscopic irreversibility. The inhomogeneous term represents the drift, or Liouville, term of the Boltzmann equation, in the first Chapman-Enskog approximation. We introduce vector notation to write the equation as

$$|\chi\rangle=H|v\rangle,$$

and define a "transport coefficient":

$$\mathcal{K}=\langle\chi|v\rangle=\sum_q \chi_q v_q. \tag{2}$$

We also introduce a scalar parameter λ, satisfying $\lambda\geq h_{\max}$, so that $\lambda-H$ is also a positive definite or positive semidefinite operator. By repeated operation with $\lambda-H$ on the Boltzmann equation (1), we define a sequence of equations

$$|\chi_m\rangle=H_m|v\rangle, \tag{3}$$

with

$$|\chi_m\rangle=(\lambda-H)^m|\chi\rangle,$$
$$H_m=(\lambda-H)^m H,$$

and define $\mathcal{K}_m=\langle\chi_m|v\rangle$, $m=0, 1, 2, \ldots$.

For a variational trial function $|u\rangle$ approximating the solution $|v\rangle$, we define the functional

$$F_m(\lambda; u)=2\langle\chi_m|u\rangle-\langle u|H_m|u\rangle. \tag{4}$$

For $m=0$, this is the functional originally used by Leibfried and Schlömann.[3] We write $|u\rangle=|v\rangle+|\delta u\rangle$ and expand F_m around the exact solution $|v\rangle$:

$$F_m(\lambda; v+\delta u)=2\langle\chi_m|v\rangle+2\langle\chi_m|\delta u\rangle-\langle u|H_m|v\rangle$$
$$-2\langle v|H_m|\delta u\rangle-\langle\delta u|H_m|\delta u\rangle.$$

Using (3), the first and third terms can be consolidated, and the second and fourth terms cancel, to give

$$F_m(\lambda; v+\delta u)=\mathcal{K}_m-\langle\delta u|H_m|\delta u\rangle. \tag{5}$$

H_m is positive (semi) definite; thus F_m is stationary about its maximum value $F_m(\lambda; v)=\mathcal{K}_m$.

The next step is to express $\mathcal{K}_m$ in terms of $\mathcal{K}_0\equiv\mathcal{K}$. We have

$$\mathcal{K}_m=\langle\chi_m|v\rangle=\langle\chi|(\lambda-H)^{m-1}(\lambda-H)|v\rangle$$
$$=\lambda\langle\chi_{m-1}|v\rangle-\langle\chi_{m-1}|H|v\rangle$$

or

$$\mathcal{K}_m=\lambda\mathcal{K}_{m-1}-\langle\chi_{m-1}|\chi\rangle=\lambda\mathcal{K}_{m-1}-\langle\chi|(\lambda-H)^{m-1}|\chi\rangle.$$

Treated as a difference equation, this has the solution

$$\mathcal{K}_m=\lambda^m\left[\mathcal{K}-\lambda^{-1}\langle\chi|\sum_{l=0}^{m-1}\left(\frac{\lambda-H}{\lambda}\right)^l|\chi\rangle\right]. \tag{6}$$

By substituting Eq. (6) for $\mathcal{K}_m$ into (5) and rearranging terms, we obtain

$$\mathcal{K}=\lambda^{-m}F_m(\lambda; u)+\lambda^{-1}\langle\chi|\sum_{l=0}^{m-1}\left(\frac{\lambda-H}{\lambda}\right)^l|\chi\rangle$$
$$+\langle\delta u|\left(\frac{\lambda-H}{\lambda}\right)^m H|\delta u\rangle. \tag{7}$$

The "remainder term" involving $|\delta u\rangle$ is positive; consequently, the sum of the first two terms is a lower bound $\mathcal{K}_m^<$:

$$\mathcal{K}\geq\mathcal{K}_m^<(\lambda; u), \quad m=0, 1, 2, \ldots$$
$$\mathcal{K}_m^<(\lambda; u)=2\langle\chi|\left(\frac{\lambda-H}{\lambda}\right)^m|u\rangle-\langle u|\left(\frac{\lambda-H}{\lambda}\right)^m H|u\rangle$$
$$+\lambda^{-1}\langle\chi|\sum_{l=0}^{m-1}\left(\frac{\lambda-H}{\lambda}\right)^l|\chi\rangle. \tag{8}$$

Formally, the terminating geometric series in the third term in (8) may be summed:

$$\lambda^{-1}\langle\chi|\sum_{l=0}^{m-1}\left(\frac{\lambda-H}{\lambda}\right)^l|\chi\rangle$$
$$=\langle\chi|\left[1-\left(\frac{\lambda-H}{\lambda}\right)^m\right]H^{-1}|\chi\rangle; \tag{9}$$

the form (8) shows, however, that H need never be explicitly inverted. In physical problems the inverse of the full collision operator does not exist, since conservation laws give rise to eigenvectors of the operator

with eigenvalue zero. Nevertheless $H^{-1}|\chi\rangle$ exists, since in any damped transport process $|\chi\rangle$ is orthogonal to these eigenvectors.

Using (9) for the third term in (8), it is easy to show that $\mathcal{K}_m^<$ satisfies the recursion relation

$$\mathcal{K}_{m+1}^< = \mathcal{K}_m^< + \lambda^{-1}\langle\xi|\left(\frac{\lambda-H}{\lambda}\right)^m|\xi\rangle, \qquad (10)$$

with $|\xi\rangle = |\chi\rangle - H|u\rangle$.

The sequence $\mathcal{K}_m^<$ is thus monotonically increasing; it must necessarily converge. To show that it converges to the *exact* transport coefficient $\mathcal{K}$, it seems necessary to assume completeness of the eigenvectors $|h_i\rangle$ of H. This allows us, for instance, to expand the error $|\delta u\rangle$ in the trial function as

$$|\delta u\rangle = \sum_i c_i|h_i\rangle;$$

the sum over eigenstates includes an integration over any continuous part of the spectrum. The remainder term in Eq. (7) is then

$$\langle\delta u|[(\lambda-H)/\lambda]^m H|\delta u\rangle = \sum_i |c_i|^2 h_i(1-h_i/\lambda)^m,$$

which approaches zero for large m. This result also shows that in order to obtain a bound $\mathcal{K}_m^<$ close to $\mathcal{K}$, it is important that the spectral expansion coefficients of the trial function $|u\rangle$ be closest to those of the exact solution in the small-eigenvalue end of the spectrum; because of the weighting factors $(1-h_i/\lambda)^m$ one can tolerate more error near the top of the spectrum. Physically this is reasonable; since the large-eigenvalue components of a disturbance from equilibrium decay most rapidly they should not dominate a transport process.

It is easy to include *one* variational parameter in the trial function $|u\rangle$; we simply replace $|u\rangle$ by $a|u\rangle$ in the bounds (8), and choose a by maximizing $\mathcal{K}_m^<(\lambda; au)$ with respect to this parameter. The results for $m=0,1$ are

$$\mathcal{K}_0^<(\lambda; au) = \langle\chi|u\rangle^2/\langle u|H|u\rangle, \qquad (11)$$

$$\mathcal{K}_1^<(\lambda; au) = \frac{\langle\chi|1-H/\lambda|u\rangle^2}{\langle u|(1-H/\lambda)H|u\rangle} + \frac{1}{\lambda}\langle\chi|\chi\rangle. \qquad (12)$$

These bounds are now independent of the normalization of $|u\rangle$. Equation (11) is the variational principle of Kohler,[1] Sondheimer,[2] and Ziman.[5]

In order to apply the bounds $\mathcal{K}_m^<$, it is necessary to choose a value for the parameter λ as well as choosing a trial function. For a collision operator whose spectrum is *not* bounded, the only possible choice is $\lambda=\infty$; in this case $\mathcal{K}_m^< = \mathcal{K}_0^<$ for all m. For phonons with cubic anharmonic interactions, we have been able to obtain a finite value $\lambda > h_{\max}$ (thus proving boundedness of the spectrum) without great difficulty. We found it very helpful to realize that one need not discuss the spectrum of the *full* collision operator, but only of the projection of the operator onto the subspace of its eigenvectors which are not orthogonal to the inhomogeneous term $|\chi\rangle$.

In the case of a collision operator with a gap in its spectrum above the zero eigenvalue, one can also choose $0<\lambda\leq h_{\min}$. The operator $\lambda-H$ is then negative definite, and the treatment above is correct with the signs of some of the inequalities reversed. From terms with even m, one obtains a sequence of lower bounds, while terms with odd m give a sequence of *upper* bounds. However, both sequences diverge, so that only the $m=0$ and $m=1$ terms are interesting. The upper bound for $m=1$ is not new; it has been obtained by Jensen, Smith, and Wilkins.[6]

III. LINEARIZED PHONON BOLTZMANN EQUATION

The Hamiltonian of a crystal including three-phonon interactions can be written in the form

$$\mathcal{H} = \sum_q \hbar\omega_q a_q^\dagger a_q + \sum_{qq'q''} \Phi_{qq'q''}(a_q - a_{-q}^\dagger)(a_{q'} - a_{-q'}^\dagger)(a_{q''} - a_{-q''}^\dagger),$$

where $a_q^\dagger$ is the creation operator of an harmonic phonon of wavevector $\mathbf{q}$, polarization s, and frequency $\omega_q(\equiv\omega_{qs})$. The cubic anharmonic coefficients $\Phi_{qq'q''}$ contain the lattice Kronecker delta function $\Delta(\mathbf{q}+\mathbf{q}'+\mathbf{q}'')$.

Under certain assumptions it is possible to derive a kinetic equation[9,10] for the single-phonon occupation number N_q. We shall deal with this phonon Boltzmann equation in the form

$$\partial N_q/\partial t + \mathbf{c}_q\cdot\nabla_r N_q = G[N_q(\mathbf{r},t)], \qquad (13)$$

where $\mathbf{c}_q$ is the group velocity $\partial\omega_q/\partial\mathbf{q}$, and the collision term $G[N_q]$ gives the change $\partial Nq/\partial t$ due to the three-phonon interactions in the above Hamiltonian. We introduce deviations $n_q = N_q - N_q^{(0)}$ from the equilibrium occupation number distribution

$$N_q^{(0)} = [\exp(\beta\hbar\omega_q)-1]^{-1},$$

and use a Master equation to relate the collision term to three-phonon scattering matrix elements of ordinary second-order perturbation theory. The results,[11] when

[9] R. Peierls, Ann. Physik **3**, 1055 (1929).
[10] C. Horie and J. A. Krumhansl, Phys. Rev. **136**, A1397 (1964); W. Götze and K. Michel, *ibid.* **157**, 738 (1967); L. J. Sham, *ibid.* **156**, 494 (1967).
[11] Reference 4, pp. 290ff.

linearized in the n's, can be written in the form

$$G[n_q]=-\sum_{q'q''}F_{qq'q''}[\delta(\omega+\omega'-\omega'')+\delta(\omega+\omega''-\omega')+\delta(\omega-\omega'-\omega'')]\sinh^2(\tfrac{1}{2}\beta\hbar\omega_q)n_q-\sum_{q'q''}2F_{qq'q''}\times[\delta(\omega+\omega''-\omega')(-n_{-q'})+\delta(\omega+\omega-\omega'')n_{q'}+\delta(\omega-\omega'-\omega'')(-n_{-q'})]\sinh^2(\tfrac{1}{2}\beta\hbar\omega_{q'}) \quad (14a)$$

$$=\sum_{q'}G_{qq'}n_{q'}. \quad (14b)$$

In this equation we have introduced

$$F_{qq'q''}=\frac{\pi}{2\hbar^2}\frac{|\Phi_{qq'q''}|^2}{\sinh(\frac{1}{2}\beta\hbar\omega)\sinh(\frac{1}{2}\beta\hbar\omega')\sinh(\frac{1}{2}\beta\hbar\omega'')},$$

and the index $-q'$ denotes $(-\mathbf{q}', s')$. Equations (14) define the linear collision operator $G_{qq'}$. We next list some of the properties of this operator:

(i) G is negative semidefinite[11]; i.e.,

$$(v,Gv)\equiv\sum_{qq'}v_qG_{qq'}v_{q'}\leq 0$$

for any distribution v_q. Equality holds only for the distribution $v_q^{(0)}=\omega_q\sinh^{-2}(\frac{1}{2}\beta\hbar\omega_q)$; this follows from the property that the phonon interactions conserve energy. Consequently, the eigenvalues of G are all negative, except for a nondegenerate eigenvalue zero. These properties result from the introduction of irreversibility through the use of a Master equation, alluded to above.

(ii) G has the formal structure

$$G[v_q]=-\Gamma_qv_q+\sum_{q'}P_{qq'}v_{q'}.$$

The Γ term is given by the first sum in Eq. (14a), and in various parlances is called the "singular" or "diagonal" or "collision rate" term. The "regular" or "off-diagonal" term with kernel P is given by the second sum in Eq. (14a).

(iii) The Γ_q are all positive (or zero); this follows since all $F_{qq'q''}\geq 0$. The elements $P_{qq'}$ are not in general all of the same sign, but note from (14a) that if n_q is an odd function of the wave vector, so that $-n_{-\mathbf{q}s}=n_{\mathbf{q}s}$, then the coefficient of $n_{q'}$ in the second sum in (14a) is always nonpositive. Stated differently: The projection of the collision operator G onto the subspace of odd distributions is an operator with nonpositive matrix elements.

(iv) Part or all of the eigenvalue spectrum of G is continuous, since the eigenvalues and eigenfunctions of the singular operator Γ_q are simply $\Gamma_{q'}$ and the delta-functions $\Delta(\mathbf{q}-\mathbf{q}')\delta_{ss'}$. $\Gamma_{q'}$ varies quasicontinuously over the Brillouin zone from zero to some finite positive value. One anticipates from knowledge of spectra of collision operators in gases[7] that the addition of the regular operator P to $-\Gamma$ to form G does not shift this continuum, adding only a bounded set of discrete eigenvalues. However, the non-square-integrable delta functions of frequency in (14a) prevent simple proof of these assertions.

In the presence of a temperature gradient ∇T, the steady-state value of the left-hand side of the phonon Boltzmann equation (13) can be linearized by replacing

$$\mathbf{c}_q\cdot\nabla_rN_q\simeq\mathbf{c}_q\cdot\nabla T\frac{\partial N_q^{(0)}}{\partial T}=\frac{\hbar\omega_q}{4kT^2}\frac{\mathbf{c}_q\cdot\nabla T}{\sinh^2(\frac{1}{2}\beta\hbar\omega_q)}.$$

Finally, the equation can be put in the form discussed in Sec. II:

$$\chi_q=\sum_{q'}H_{qq'}v_{q'},$$

where

$$v_q=n_q\sinh(\tfrac{1}{2}\beta\hbar\omega_q),$$
$$H_{qq'}=-4k[\sinh(\tfrac{1}{2}\beta\hbar\omega_q)/\sinh(\tfrac{1}{2}\beta\hbar\omega_{q'})]G_{qq'}, \quad (14c)$$
$$\chi_q=-(\hbar\omega_q/T^2)\mathbf{c}_q\cdot\nabla T/\sinh(\tfrac{1}{2}\beta\hbar\omega_q).$$

H is symmetric and positive semidefinite; the eigenvalues of H and G differ only by a constant factor $-4k$. Because of property (iii) above, the projection of H onto the subspace of odd functions is an operator with non-negative matrix elements. In fact, one need consider only such a projected operator, because the solution v_q is an odd function, and we shall require that any trial solution approximating v_q also satisfy this symmetry property. One sees that v_q is odd as follows: The Boltzmann equation may also be written

$$\chi_{-q}=\sum_{q'}H_{-q,q'}v_{q'}=\sum_{q'}H_{-q,-q'}v_{-q'}.$$

Because the group velocity is an odd function, so is χ_q, and from (14a) one has $H_{-q,-q'}=H_{qq'}$. Thus,

$$\chi_q=\sum_{q'}H_{qq'}(-v_{-q'}).$$

Then $v_{q'}$ and $-v_{-q'}$ satisfy the same equation; since the solution to the equation is unique if the temperature is specified, we conclude that $v_q=-v_{-q}$.

To compute the lattice thermal conductivity, one introduces the lattice energy flux $\mathbf{Q}$, given by[9,12]

$$\mathbf{Q}=\frac{1}{V}\sum_q\hbar\omega_q\mathbf{c}_qn_q=-K(T)\nabla T.$$

Here V is the volume of the crystal. The second equality is Fourier's (phenomenological) law defining the thermal conductivity $K(T)$. We treat only the case of a cubic crystal, so that K is a scalar. This definition allows one to define a "reduced" thermal conductivity:

$$\mathcal{K}\equiv KV\left(\frac{\nabla T}{T}\right)^2=\sum_q\chi_qv_q=\langle\chi|v\rangle. \quad (15)$$

[12] R. J. Hardy, Phys. Rev. **132**, 168 (1963).

IV. UPPER BOUND FOR LARGEST EIGENVALUE OF H

In this section we present one way of approaching the question of the boundedness of the spectrum of the phonon collision operator. Briefly, the procedure is to regard the operator as a limiting case of a matrix operator to which the theorem of Perron and Frobenius[13] can be applied.

The Perron-Frobenius theorem concerns the maximum eigenvalue of a non-negative irreducible matrix M, where "non-negative" means all elements $M_{ij} \geq 0$, and the irreducibility need be only with respect to a restricted set of operations, the permutations of the row and column indices of M. The consequence of the theorem which we shall use is[14] that the largest eigenvalue of M is less than the largest of the row sums $\sum_j M_{ij}$.

To apply this result we formally consider a finite crystal of volume V containing N particles and satisfying periodic boundary conditions. The first Brillouin zone of the crystal thus contains a finite number of points, and the collision operator $H_{qq'}$ can be treated as a matrix operator of finite dimensionality. As pointed out above, $H_{qq'}$ is non-negative if one considers only odd trial functions. The irreducibility property we regard as providing a restriction on what lattice models may be used. Physically it means that it should be impossible to divide the phonons into two disjoint sets such that no phonon of one set interacts via anharmonicity with any phonon of the other set. Any reasonable model should exhibit this irreducibility, in order that the lattice in equilibrium be characterized by a single temperature.

Thus for a finite crystal we can bound the spectrum of the (projected) collision operator from above with a parameter λ set equal to the largest of the row sums $\sum_{q'} H_{qq'}$. We proceed to the limit of an infinite crystal by first replacing $\sum_{q'}$ by $V/(2\pi)^3 \sum_{s'} \int d\mathbf{q}'$, and then letting N, $V \to \infty$, holding N/V constant. For the Debye model introduced in Sec. V, one can verify virtually by inspection that the largest row sum stays finite in this limit. In the general case of a phonon spectrum with anisotropy and dispersion, the proof that the row sums stay finite is given in the Appendix. In the Appendix we also examine the behavior of the largest row sum for an infinite crystal in the limit of low temperatures. It is shown there that as $T \to 0°\mathrm{K}$, the contribution comes entirely from the largest of the diagonal terms H_{qq}, which is also shown to be independent of temperature, at low temperatures. From Sec. III, the diagonal elements of H are simply related to the phonon relaxation rates Γ_q, which contribute a continuum to the spectrum of the collision operator:

$$H_{qq} = -4kG_{qq} = 4k\Gamma_q .$$

Thus at least at zero temperature there are no eigenvalues of H above the top of the continuum. This feature may be present at all temperatures, but the methods used here are too weak to prove it, since in this application the Perron-Frobenius theorem gives only an inequality for the largest eigenvalue.

TABLE I. Maximum relaxation rates and row sums. The unit of the last two columns is $(kq_D c_t)(k\Theta/mc_t^2)(0.0474\gamma^2)(3\pi)$.

T/Θ_t	$4k\Gamma_{\max}$	λ
0	30.3	30.3
1/20	30.5	31.0
1/18	30.6	31.2
$\frac{1}{16}$	30.6	31.4
$\frac{1}{12}$	30.8	32.3
$\frac{1}{8}$	31.4	35.3
$\frac{1}{4}$	35.3	49.8
$\frac{1}{2}$	49.8	87.1
1	87.1	168
2	168	332
10	828	1655

V. CALCULATIONS FOR DEBYE MODEL

It is of considerable practical importance to discover just how rapidly the sequence of bounds $\mathcal{K}_m^<$ of Sec. II converges in a typical application. Toward this end, we have computed $\mathcal{K}_1^<$ and the Ziman bound $\mathcal{K}_0^<$ [Eqs. (11) and (12)], for a simplified lattice model for which the energy and wave-vector conservation laws built into the matrix elements of H do not cause too extreme complications. The model is that of a three-dimensional isotropic elastic continuum. The phonon spectrum contains two degenerate transverse branches with frequencies

$$\omega_{\mathbf{q}t} = c_t |\mathbf{q}| ,$$

and a longitudinal branch with frequencies

$$\omega_{\mathbf{q}l} = c_l |\mathbf{q}| , \quad c_l/c_t = 1.76 .$$

The ratio c_l/c_t was chosen to be that for a classical cubic crystal with nearest-neighbor central forces. For the cubic anharmonic coefficients, we use[15]

$$|\Phi_{qq'q''}|^2 = \frac{0.0474}{N} \frac{\hbar^3\gamma^2}{mc_t^2} \omega_q \omega_{q'} \omega_{q''} \Delta(\mathbf{q}+\mathbf{q}'+\mathbf{q}'') ,$$

where γ is the Grüneisen constant and Nm the total crystal mass. The first Brillouin zone is replaced by a Debye sphere of radius $q_D = (6\pi^2 N/V)^{1/3}$; N/V is the particle density.

We include umklapp processes through the device suggested by Hamilton and Parrott.[16] For the umklapp process $(\mathbf{q}s)+(\mathbf{q}'s') \rightleftharpoons (-\mathbf{q}''s'')$, the only allowed value

[13] See, e.g., F. R. Gantmacher, *Applications of the Theory of Matrices* (Interscience Publishers, Inc., New York, 1959), Chap. III.

[14] Reference 13, p. 76.

[15] Reference 3, p. 83; Ref. 5, p. 295.

[16] R. Hamilton and J. Parrott, Phys. Rev. **178**, 1284 (1969).

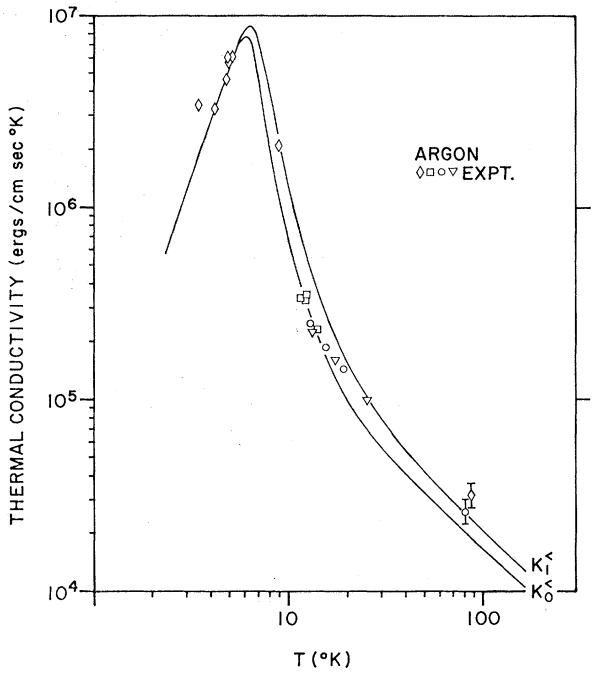

FIG. 1. Thermal conductivity of solid argon. Solid lines are the lower-bound calculations reported here. Experimental data taken from Ref. 18.

for the reciprocal-lattice vector $\mathbf{G}=\mathbf{q}+\mathbf{q}'+\mathbf{q}''$ is defined to be the vector of magnitude $2q_D$ directed along $\mathbf{q}+\mathbf{q}'$.

The allowed three-phonon interactions (both normal and umklapp) for this model are

$$l+l''\rightleftharpoons l',\quad l\rightleftharpoons l''+l',\quad l\rightleftharpoons l''+l'.$$

In addition, the normal-process interactions between three colinear phonons of the same polarization, $l+l''\rightleftharpoons l'$ and $t+t''\rightleftharpoons t'$, are also allowed, but become forbidden when dispersion is added to the phonon spectrum. We have thus simply ignored the contributions of these extra two processes in all calculations.

In order to determine the largest of the row sums $\sum_{q'}H_{qq'}$, we have evaluated these sums for both polarizations over the entire Debye sphere, for 10 temperatures between $\Theta_t/20$ and $10\,\Theta_t$, where Θ_t is the transverse Debye temperature $\hbar c_t q_D/k$. The computations were performed in the limit of an infinite crystal. In all cases the largest row sum occurs for the longitudinal mode at $q=q_D$, i.e., the mode of highest frequency. We call this row sum λ ($\lambda>h_{\max}$). We have also computed the spectrum of relaxation rates, the quantities $4k\Gamma_q$ of Sec. III. One anticipates that these quantities define the continuous part of the eigenvalue spectrum of H, but see the remarks under property (iv) of Sec. III. At all temperatures, $4k\Gamma_q$ was found to vary continuously from zero for $q=0$ to a maximum value which occurs for the longitudinal mode at $q=q_D$. Table I shows $4k\Gamma_{\max}$ and λ.

In the limit $T/\Theta\rightarrow\infty$, one can show that $\lambda/(4k\Gamma_{\max})\rightarrow 2$; this behavior is seen in Table I. The low-temperature results show that, in accordance with the conclusions of the Appendix, λ converges toward $4k\Gamma_{\max}$ from above.

Taking the parameter λ from Table I, we have computed the lower bounds $\mathcal{K}_0^<$ and $\mathcal{K}_1^<$ of Sec. II, and the quantities with the dimensions of thermal conductivity defined from them via Eq. (15). These conductivities we label $K_0^<$ and $K_1^<$; they are listed in Table II. In both cases the trial function used was the displaced Planck function

$$u_q=-\mathbf{q}\cdot\nabla T/\sinh(\tfrac{1}{2}\beta\hbar\omega_q). \tag{16}$$

The numerical computations involved nothing more sophisticated than the evaluation of two-dimensional integrals of a function given in analytic form.

From Table II one sees that the relative difference between $K_1^<$ and $K_0^<$ ranges from more than 20% at very high temperatures to almost 90% at low temperatures. Thus the new bound $K_1^<$ is a considerable improvement over the Ziman bound $K_0^<$, which has been the basis for previous variational calculations of lattice thermal conductivity.

TABLE II. Lower bounds for lattice thermal conductivity. The unit of thermal conductivity is $K=(kq^2{}_Dc_t)(mc_t^2/k\Theta)\times[(1.76)^2/0.0474\gamma^2](1/162\pi^3)$.

T/Θ_t	$K_0^</K$	$K_1^</K$	$K_1^</K_0^<$
1/20	3.79×10^5	7.10×10^5	1.87
1/18	6.06×10^4	1.13×10^5	1.87
1/16	1.05×10^4	1.96×10^4	1.86
1/12	440	812	1.85
1/8	34.4	61.9	1.80
1/4	5.36	8.35	1.56
1/2	2.27	3.03	1.33
1	1.14	1.44	1.26
2	0.577	0.713	1.24
10	0.116	0.142	1.22

VI. APPLICATION TO SOLID ARGON

It is possible that the considerable difference found between the bounds $K_0^<$ and $K_1^<$ for lattice thermal conductivity is a consequence of the Debye model for which the calculations were performed, and will be diminished for a more realistic model including anisotropy and dispersion in the phonon spectrum. We have not examined this directly; rather, we have tested the over-all adequacy of the model by comparing its predictions with measurements for solid argon. We have done this first by choosing appropriate values for the model parameters γ, c_t and the lattice constant.[17] It is also desirable to include in the model the possibility of scattering from the boundaries of a finite crystal. Ziman[5] has discussed the theory of boundary scattering; we have simulated his conclusions by adding to the

[17] O. G. Peterson, D. N. Batchelder, and R. O. Simmons, Phys. Rev. **150**, 703 (1966).

collision operator $H_{qq'}$ a constant diagonal term $4k(c/L)\delta_{qq'}$. Typically, c should be an averaged sound velocity and L a crystal dimension. We have adopted the value 7.8×10^6 sec^{-1} for c/L by unsystematically fitting the low-temperature thermal conductivity data for argon. This is the only adjustable parameter in the calculation. This addition of boundary scattering makes a negligible contribution to λ; it is also negligible in both bounds $K_0^<$ and $K_1^<$ for argon above about 7°K.

The bounds for argon are shown in Fig. 1, along with the results of several different experimental investigations.[18] It is not surprising that on the low-temperature side of the conductivity maximum the two bounds are identical, for in this region boundary scattering dominates, and the displaced Planck function (16) is the exact solution of the Boltzmann equation.

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APPENDIX

First we wish to show that the row sums of the phonon collision matrix are finite, in the limit of an infinite crystal. For a finite crystal, these sums are

$$\sum_{q'} H_{qq'} = \frac{2\pi k}{\hbar^2} \sum_{q''q'} \left\{ |\Phi_{qq'q''}|^2 \times \frac{\sinh(\frac{1}{2}\beta\hbar\omega)+\sinh(\frac{1}{2}\beta\hbar\omega')+\sinh(\frac{1}{2}\beta\hbar\omega'')}{\sinh(\frac{1}{2}\beta\hbar\omega')\sinh(\frac{1}{2}\beta\hbar\omega'')} \right\} \times[\delta(\omega+\omega'-\omega'')+\delta(\omega+\omega''-\omega')+\delta(\omega-\omega'-\omega'')], \tag{A1}$$

which follows from Eqs. (14a) and (14c). In the sum of three sinh's in the numerator of the bracketed factor, the term with argument $\frac{1}{2}\beta\hbar\omega\equiv\frac{1}{2}\beta\hbar\omega_q$ represents the contribution of the diagonal term H_{qq}, while the other two terms together give the off-diagonal contributions to the row sum. We write the cubic anharmonic coefficients in the form

$$|\Phi_{qq'q''}|^2=(1/N)|\phi_{qq'q''}|^2\Delta(\mathbf{q}+\mathbf{q}'+\mathbf{q}''),$$

where $\Delta(\mathbf{q}+\mathbf{q}'+\mathbf{q}'')$ is the lattice Kronecker delta function, and $\phi_{qq'q''}$ is independent of particle number N. The coefficients $|\Phi|^2$ must always depend on particle number in this fashion, in order that the cubic anharmonic Hamiltonian be an extensive quantity. In addition, one can show that $|\phi_{qq'q''}|^2$ is bounded, and that for one of the wave vectors (say, $\mathbf{q}''$) small compared to the lattice constant a_0, it has the form[19]

$$|\phi_{qq'q''}|^2=|\mathbf{q}''|\cdot F(\mathbf{q}s,\mathbf{q}'s',\hat{\mathbf{q}}''s'')+O((q''/a_0)^2), \tag{A2}$$

where $\hat{\mathbf{q}}''$ is a unit vector in the direction of $\mathbf{q}''$. If in addition $|\mathbf{q}'|$ and/or $|\mathbf{q}|$ are small, then $|\phi_{qq'q''}|^2$ depends linearly upon the magnitudes of the other small wave vectors as well. This dependence ensures that there are no singularities of the factor in brackets in Eq. (A1) due to zeros of the denominator at $\mathbf{q}',\mathbf{q}''=0$. The bracket thus satisfies

$$\{\cdots\}<(\text{const}/N)\Delta(\mathbf{q}+\mathbf{q}'+\mathbf{q}''),$$

so that

$$\sum_{q'} H_{qq'} < \frac{\text{const}}{N} \sum_{q'} [\delta(\omega+\omega'-\omega'')+\delta(\omega+\omega''-\omega')+\delta(\omega-\omega'-\omega'')],$$

where $\omega''=\omega''(\mathbf{q}+\mathbf{q}')$.

For a crystal of infinite volume, we replace $N^{-1}\sum_{\mathbf{q}'}$ by $v/(2\pi)^3\int d\mathbf{q}'$, where v is the volume per particle. Thus to prove boundedness of the row sums in this limit, it is sufficient to show the boundedness of the integrals

$$\int d\mathbf{q}'\delta(\omega(\mathbf{q})\pm\omega'(\mathbf{q}')-\omega''(\mathbf{q}+\mathbf{q}')), \tag{A3}$$

which are of the form

$$\int_{f(\mathbf{q}')=\omega} dS'|\nabla' f(\mathbf{q}')|^{-1}\equiv G(\omega,\mathbf{q}), \tag{A4}$$

where $f(\mathbf{q}')\equiv\omega''(\mathbf{q}+\mathbf{q}')\mp\omega'(\mathbf{q}')$, and the integral is over the portion of the surface $f(\mathbf{q}')=\omega$ lying within the Brillouin zone of $\mathbf{q}'$. The integral (A3) is then $G(\omega,\mathbf{q})$ at $\omega=\omega(\mathbf{q})$, but we shall show that $G(\omega,\mathbf{q})$ is bounded for *all* ω. The area of the surface S' is finite; if the integrand is bounded on the surface, the integrals are then finite. However, because $f(\mathbf{q}')$ is a continuous periodic function of $\mathbf{q}'$, there must exist critical points in the Brillouin zone of $\mathbf{q}'$ at which the gradient in (A4) is zero, and for special values of ω some of these points may lie on the surface of integration. The critical points are of course exact analogies of van Hove critical points in the phonon density-of-states integral,[20] and in fact van Hove's analysis of that function may be applied outright to (A4). The conclusion is that $G(\omega,\mathbf{q})$ is bounded and continuous in ω for every $\mathbf{q}$, possessing infinite discontinuities in the *slope* $\partial G/\partial\omega$ at some points. The boundedness of $G(\omega,\mathbf{q})$ implies that the row sums, and consequently the eigenvalue spectrum, of the collision operator are finite.

[18] G. K. White and S. B. Woods, Phil. Mag. **3**, 785 (1958); D. Lawrence, A. Stewart, and E. Guptill, Can. J. Phys. **37**, 1069 (1959); A. Berne, G. Boato, and M. DePaz, Nuovo Cimento **46B**, 182 (1966).

[19] This is most easily proven from the expression given by Leibfried, Ref. 4, p. 299, Eq. (91.16).

[20] L. van Hove, Phys. Rev. **89**, 1189 (1953).

In the low-temperature limit, we can also show that the contribution to each of the row sums comes entirely from the diagonal term in the sum. The implications of this property are discussed in Sec. IV of the text. We first show that the sum of the off-diagnal terms in a row vanishes like $O(T^3)$ as $T\to 0°K$. This latter sum is the right-hand side of (A1), with the $\sinh(\frac{1}{2}\beta\hbar\omega_q)$ term in the numerator of the factor in brackets omitted:

$$\sum_{q'\neq q} H_{qq'} = \frac{2\pi k}{\hbar^2}\sum_{q''q'}\left\{|\Phi_{qq'q''}|^2\frac{2}{\sinh(\frac{1}{2}\beta\hbar\omega'')}\right\} \times[\delta(\omega+\omega'-\omega'')+\delta(\omega+\omega''-\omega') +\delta(\omega-\omega'-\omega'')], \quad \text{(A5)}$$

where we have used the symmetry of the right-hand side of (A1) under permutation of q' and q''. We thus wish to examine the temperature dependence of integrals like

$$\int d\mathbf{q}'\frac{|\Phi_{qq'q''}|^2}{\sinh(\frac{1}{2}\beta\hbar\omega'')}\delta(\omega\pm\omega'-\omega'') = \int dS'\frac{|\Phi_{qq'q''}|^2}{\sinh[\frac{1}{2}\beta\hbar(\omega(\mathbf{q})\pm\omega'(\mathbf{q}'))]} \times|\pm\nabla'\omega'(\mathbf{q}')-\nabla'\omega''(\mathbf{q}+\mathbf{q}')|^{-1}, \quad \text{(A6)}$$

where $\mathbf{q}''=\mathbf{G}-\mathbf{q}-\mathbf{q}'$, $\mathbf{G}$ is a reciprocal-lattice vector, and $\omega(\mathbf{q})\pm\omega'(\mathbf{q}')=\omega''(\mathbf{q}+\mathbf{q}')$ on the surface S'. We consider only those row sums for which $\frac{1}{2}\beta\hbar\omega(\mathbf{q})\gg 1$; at low enough temperatures this includes most of the phonons in the zone, and inclusion of the remaining modes does not affect the conclusions. In this case, the integral in (A6) with the (+) sign will vanish like $\exp[-\frac{1}{2}\beta\hbar\omega(\mathbf{q})]$, and we need consider in more detail only the integral with the (−) sign, corresponding to attenuation of the mode q by emission of two phonons. The integrand is sizable only where

$$\tfrac{1}{2}\beta\hbar(\omega(\mathbf{q})-\omega'(\mathbf{q}'))=\tfrac{1}{2}\beta\hbar\omega''(\mathbf{q}+\mathbf{q}')\lesssim 1;$$

at low enough temperatures this will require that ω'' be in the low-frequency acoustic range, where

$$\omega''(\mathbf{q}+\mathbf{q}')\approx c''|\mathbf{q}+\mathbf{q}'-\mathbf{G}|,$$

with c'' some angular-averaged sound velocity. Thus the major contribution to the integral (A6) comes from that portion of the surface S' on which

$$|\mathbf{q}''|=|\mathbf{q}+\mathbf{q}'-\mathbf{G}|\lesssim 2kT/\hbar c''.$$

The area of this portion of S' is of order $q''^2=O(T^2)$. Since q'' is small over this area, the dependence (A2) holds for the cubic anharmonic coefficients, so that the integrand is of order T over the contributing area. We conclude that the off-diagonal sums

$$\sum_{q'\neq q} H_{qq'}$$

vanish at least like $O(T^3)$, and exponentially rapidly for those modes for which spontaneous emission processes are forbidden.

Exactly the same sort of analysis can be applied to the diagonal terms H_{qq}. These are given by the right-hand side of (A5), with the replacement

$$\frac{2}{\sinh(\frac{1}{2}\beta\hbar\omega'')}\to\frac{\sinh(\frac{1}{2}\beta\hbar\omega)}{\sinh(\frac{1}{2}\beta\hbar\omega')\sinh(\frac{1}{2}\beta\hbar\omega'')}.$$

As above, for absorption processes this factor is exponentially small in T. For emission processes it is *independent* of β over most of the surface S', excluding only the portion discussed above, which gives a contribution of order T^3. This result is merely an expression of the fact that even at $T=0°$K those modes which can decay by spontaneous emission will have a finite lifetime.

In summary, then,

(a) the eigenvalue spectrum of the (projected) phonon collision operator is bounded, and

(b) at low temperatures

$$(\sum_{q'} H_{qq'})_{\max}-(H_{qq})_{\max}=O(T^3),$$

$$(H_{qq})_{\max}=\text{const}+O(T^3).$$

At low temperatures we would expect the largest row sum to occur for a longitudinal mode with wave vector near the edge of the Brillouin zone, since for such modes the possibilities for emission processes, both normal and umklapp, are most numerous.