Solution of the Linearized Phonon Boltzmann Equation*

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The linearized Boltzmann equation for the pure phonon field may be solved formally in terms of the eigenvectors of the normal-process collision operator. This representation is particularly convenient as a basis for solutions, since in the isotropic dispersionless case the temperature deviation δT and the heat current $\mathbf{Q}$ are related to zero-eigenvalue eigenfunctions of this operator. The formal solution is summarized by two macroscopic equations relating δT and $\mathbf{Q}$. The first of these is the usual thermal-energy conservation condition; the second is a generalized phonon-thermal-conductivity relation involving a $\mathbf{k}$- and Ω-dependent thermal conductivity $\kappa(\mathbf{k},\Omega)$. Examination of $\kappa(0,0)$ clarifies the role of normal processes and momentum-relaxing R processes in determining the steady-state heat current. An alternative to the Callaway equation for the thermal conductivity is obtained. Examination of $\kappa(\mathbf{k},\Omega)$ leads to a discussion of space-time-dependent phenomena in a phonon gas. A set of macroscopic equations which describe second sound with damping and Poiseuille flow are obtained. Second sound from the linear-response point of view discussed by Griffin is considered briefly. In the companion paper the problem of Poiseuille flow in a phonon gas is dealt with in considerable detail using these equations. The pure phonon field in a harmonic crystal is characterized by zero expectation value of the density variation of the crystal. However, in addition to the pure phonon field one may also have an elastic dilatation field in the harmonic approximation, which does lead to periodic density variation. Anharmonic effects will couple the phonon field and the dilatation field, leading to a coupling between elastic (sound waves) and thermal waves. The coupled-field dispersion relations are discussed.

INTRODUCTION

THE thermal properties of an insulating crystal at low temperature can be described in terms of the aggregate of phonons which inhabit it. These elementary excitations have complete meaning only in the harmonic approximation; however, as has been demonstrated amply both theoretically[1] and experimentally,[2] they are well-defined excitations for practical purposes even when they have a finite lifetime (e.g., in an anharmonic crystal or a crystal with defects, etc.). They constitute a useful basis to describe a variety of phenomena.

Even though the individual "quasiparticle" phonon may have a finite lifetime against decay due to anharmonic interactions, in a pure (although anharmonic) crystal the translational periodicity gives rise to certain invariants for the aggregate of phonons.[3] These invariants are associated in an intimate way with a hydrodynamic behavior of the interacting phonon system.

It is our purpose to discuss some aspects of this hydrodynamic behavior in terms of a Boltzmann equation of motion for the interacting phonon system. This description (i.e., the Boltzmann equation for interacting phonons) has somewhat limited validity. A more general approach may be developed in terms of the Green's function for the elements of the phonon density matrix[4,5] but in actual fact when the usual approximations are made it is of no greater generality than the Boltzmann method, as employed for long-wavelength collective phonon behavior to be discussed here. The physically important conservation principles may be incorporated directly when using the Boltzmann equation, and the principal features of collective behavior such as phonon hydrodynamics may be developed in this framework.

Another aspect of the problem is introduced by recalling that the lattice displacement operators in phonon representation are linear in the phonon annihilation and creation operators. In turn, their expectation for any pure phonon (number) state is zero, and the diagonal elements of the matrix representation of any linear function of the displacements e.g., the dilatation vanish in number representation. Thus an elastic dilatation or "first sound" wave in a crystal must be represented by essentially nondiagonal density matrices in phonon number representation; in fact a "coherent state" representation is required.

We are thus led in analogy to the hydrodynamic separation of convection and diffusive motions in fluids,

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to follow Landau,[6] Ehrenreich and Woodruff,[6] and others and to regard the elastic dilatational field and phonon fields separately in the harmonic approximation but coupled when anharmonicity is taken into account. The microscopic demonstration of the essential validity of this view has recently been carried through by Kwok and Martin.[5] In the present paper we examine the phonon system at both the Boltzmann equation and macroscopic level, and discuss the coupling of the two fields.

The present paper is laid out as follows: In Secs. I–IV we discuss the pure phonon field; in Sec. V we outline the anharmonic coupling to macroscopic elastic fields. In Sec. I the description of steady-state thermal conductivity is summarized with the intent of illustrating those aspects of the transport equation that are important to understanding its correct solution. In Sec. II the formal solution of the Boltzmann equation is developed in terms of the eigenvectors of the normal process collision operator. The method we have developed in detail was indicated by Peierls[7] in the cornerstone paper on this subject; he noted the singular nature of the normal process operator and suggested the separation of the distribution function into components reflecting this fact.

The results of Sec. II are applied to the case of steady-state thermal conductivity in Sec. III; the variational method of Ziman[8] is discussed, and the relaxation-time approximation of Callaway[9] is found as a special approximate case. An alternative is suggested to the Callaway expression for the thermal conductivity. The results of Sec. II are applied to the time-dependent case in Sec. IV; macroscopic equations for the temperature deviation and heat current are obtained, comparison is made with the previous work of Sussmann and Thellung.[10] In Sec. V, a phenomenological coupling between the thermal and elastic fields along the lines of the Grüneisen model is used to illustrate the anharmonic coupling between the fields, and the consequences are discussed.

I. FORMULATION OF THE PROBLEM

The quasiparticle occupation probability $n(\mathbf{q},\mathbf{x},t)$ of the phonon states may be regarded as the $\mathbf{q},\mathbf{x}$ element of the Wigner density matrix which for slow spatial variation satisfies the Boltzmann equation

$$[(\partial/\partial t)+\mathbf{v}(\mathbf{q})\cdot\boldsymbol{\nabla}-\mathbf{C}]n(\mathbf{q},\mathbf{x},t)=0. \tag{1}$$

This equation is assumed to have pointwise validity within the crystal; the collision operator $\mathbf{C}$ is "local" in coordinate space; the group velocity $\mathbf{v}(q)$ is "local" in momentum space ($\mathbf{q}$ space). In general, $\mathbf{C}$ is a nonlinear integral operator in $\mathbf{q}$ space but it may be linearized as a very good approximation. An instructive form of Eq. (1) is

$$\mathbf{D}n(\mathbf{q},\mathbf{x},t)=\mathbf{C}n(\mathbf{q},\mathbf{x},t) \tag{2}$$

where $\mathbf{D}=(\partial/\partial t)+\mathbf{v}\cdot\boldsymbol{\nabla}$, is the drift operator. Two possible procedures may be employed toward solving Eq. (2) in the linear approximation. One may solve Eq. (2) in the form

$$n=\mathbf{D}^{-1}[\mathbf{C}n], \tag{3}$$

which may be done[11] in terms of the Green's function for the operator $\mathbf{D}$, or in the form

$$n=\mathbf{C}^{-1}[\mathbf{D}n], \tag{4}$$

if the inverse of the collision operator $\mathbf{C}^{-1}$ is known. The latter is the usual approach in dealing with steady-state thermal conductivity; where typically one makes the approximation

$$\mathbf{D}n\rightarrow\mathbf{v}\cdot\boldsymbol{\nabla}N_0(T(x)),\quad N_0=[\exp(\hbar\omega/k_BT)-1]^{-1} \tag{5}$$

and deals with Eq. (4) in the form

$$n=\mathbf{C}^{-1}[\mathbf{v}\cdot\boldsymbol{\nabla}T\partial N_0/\partial T]. \tag{6}$$

Certain formal aspects of this equation have been dealt with previously.[12] The nature of the collision operator $\mathbf{C}$, which must be handled with care in solving Eq. (6), is discussed in detail there.

The main points of that discussion are:

(i) The collision operator $\mathbf{C}$ may be divided into two parts,

$$\mathbf{C}=\mathbf{N}+\mathbf{R}, \tag{7}$$

where $\mathbf{N}$ is the normal-process collision operator and $\mathbf{R}$ refers to other processes, e.g., umklapp scattering, mass-fluctuation scattering, etc.

(ii) In principle $\mathbf{C}^{-1}$ in Eq. (6) can be expressed directly in terms of its eigenvectors and eigenvalues, if these are known, subject to the existence of the inverse. Adopting a notation similar to the Dirac notation, if $\mathbf{C}|\mu\rangle=g_\mu|\mu\rangle$ is the characteristic equation for the μth eigenvectors of $\mathbf{C}$ with eigenvalue g_μ, then

$$\mathbf{C}=\sum_\mu g_\mu|\mu\rangle\langle\mu|, \tag{8}$$

and

$$\mathbf{C}^{-1}=\sum_\mu(1/g_\mu)|\mu\rangle\langle\mu|, \tag{9}$$

[6] T. O. Woodruff and H. Ehrenreich, Phys. Rev. **123**, 1553 (1961); L. Landau and F. Rumer, Physik Z. Sowjetunion **11**, 18 (1937); L. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon Press, Inc., New York, 1959), pp. 119 ff.; R. Kronig, Physica **19**, 535 (1953); A. Akhieser, J. Phys. (U.S.S.R.) **1**, 277 (1939).

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[8] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, Oxford, England, 1960), Chap. 7.

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

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[12] J. A. Krumhansl, Proc. Phys. Soc. (London) **85**, 921 (1965).

where the eigenvectors satisfy the condition $\langle\mu|\mu'\rangle=\delta_{\mu\mu'}$; the explicit meaning of the operation $\langle\mu|\mu'\rangle$ will be given below. Clearly for $\mathbf{C}^{-1}$ to exist we must have $g_\mu\neq 0$ for all μ.

(iii) In the problem at hand we do not know the eigenvectors or eigenvalues of $\mathbf{C}$ in any detail, except for the equilibrium distribution N_0 which follows from energy conservation in the collisions. However, at low temperature where $\mathbf{R}\ll\mathbf{N}$, $\mathbf{C}\simeq\mathbf{N}$; we do have partial information about the properties of $\mathbf{N}$. In particular, four distribution functions (in $\mathbf{q}$ space) are known to have eigenvalue zero as eigenvectors of the $\mathbf{N}$ operator (See Appendix A).

$$\begin{aligned}&\mathbf{N}|\eta_{1x}\rangle=0|\eta_{1x}\rangle\\ \mathbf{N}|\eta_0\rangle=0|\eta_0\rangle\quad&\mathbf{N}|\eta_{1y}\rangle=0|\eta_{1y}\rangle\\ &\mathbf{N}|\eta_{1z}\rangle=0|\eta_{1z}\rangle.\end{aligned}\tag{10}$$

As $T\to 0$, $\mathbf{R}\to 0$, these eigenvectors dominate $\mathbf{C}^{-1}$ and eventually lead to a divergence. A detailed discussion is given in Ref. 12.

A solution of Eq. (4) must be sought in the form

$$n(\mathbf{q},\mathbf{x},t)=a_0|\eta_0\rangle+\sum_{\alpha=x,y,z}a_{1\alpha}|\eta_{1\alpha}\rangle+\mathbf{C}^{-1}[(1-\mathbf{P}_0-\mathbf{P}_1)\mathbf{D}n],\tag{11}$$

where $\mathbf{P}_0=|\eta_0\rangle\langle\eta_0|$, $\mathbf{P}_1=|\eta_1\rangle\langle\eta_1|$ are projection operators introduced to orthogonalize to the null space $\{|\eta_0\rangle, |\eta_{1x}\rangle, |\eta_{1y}\rangle, |\eta_{1z}\rangle\}$ of $\mathbf{C}$. The coefficients a_0 and a_1 measure the amount of homogeneous soution in $n(\mathbf{q},\mathbf{x},t)$. These coefficients are determined through auxiliary conditions on the invariants of the collective phonon system.

This basis for solution of Eq. (4) may be employed not only in the limit where normal processes dominate $\mathbf{C}$, but also in developing a solution in the general case, provided that the set of all eigenvectors $\{|\eta_\mu\rangle\}$ is a complete set in $\mathbf{q}$ space.

(iv) The principal features of transport processes at low temperature may be conveniently discussed assuming an (a) dispersionless and (b) isotropic phonon spectrum. Under these special conditions it can be shown that a_0 and $a_{1\alpha}$ in Eq. (11) are proportional to the temperature deviation and αth heat current component, respectively (See Appendix A).

This background may be summarized: we expect that the solution of the phonon Boltzmann equation, Eq. (2), may be developed in terms of the eigenvectors of the normal process collision operator; the important information in this basis is contained in its null-space components, being the local thermal-energy density and heat current.

II. SOLUTION OF THE BOLTZMANN EQUATION

The linearized Boltzmann equation, Eq. (2), may be symmetrized[12] by using the "basis"

$$n^*(\mathbf{q},\mathbf{x},t)=n(\mathbf{q},\mathbf{x},t)2\sinh(\tfrac{1}{2}x_q),\tag{11a}$$

where $x_q=\hbar\omega_q/k_BT$; the collision operator and the drift operator are then self-adjoint. Equation (2) then becomes

$$(\mathbf{N}^*+\mathbf{R}^*)n^*=\mathbf{D}n^*,\tag{12}$$

where the self-adjoint collision operators $\mathbf{N}^*$ and $\mathbf{R}^*$ are simply related to $\mathbf{N}$ and $\mathbf{R}$.[12] The eigenvectors of the $\mathbf{N}^*$ operator (assuming isotropy and cubic symmetry) may be divided into two classes, those having zero eigenvalue and the rest. The only obvious ones of the former are (Appendix A):

$$|\eta_0\rangle\leftrightarrow\mu x_q(2\sinh\tfrac{1}{2}x_q)^{-1}\tag{13}$$

$$\left.\begin{matrix}|\eta_{1x}\rangle & \lambda_x q_x\\ |\eta_{1y}\rangle\leftrightarrow & \lambda_y q_y\\ |\eta_{1z}\rangle & \lambda_z q_z\end{matrix}\right\}(k_BT2\sinh\tfrac{1}{2}x_q)^{-1}\tag{14}$$

where λ_x, λ_y, λ_z and μ are normalization constants according to

$$\langle\eta_\alpha|\eta_\beta\rangle=V/(2\pi)^3\int d\mathbf{q}\,\eta_\alpha(\mathbf{q})\eta_\beta(\mathbf{q})=\delta_{\alpha,\beta}.\tag{15}$$

The eigenvector $|\eta_0\rangle$ has eigenvalue zero for both the normal process collision operator and the R-process collision operator as a consequence of energy conservation during phonon interaction. The eigenvectors $|\eta_{1x}\rangle$, $|\eta_{1y}\rangle$ and $|\eta_{1z}\rangle$ have eigenvalue zero for the normal process collision operator as a consequence of translational periodicity. Normal process collisions conserve momentum, R processes do not conserve momentum, the eigenvectors $|\eta_{1x}\rangle$, $|\eta_{1y}\rangle$ and $|\eta_{1z}\rangle$ are not eigenvectors of $\mathbf{R}^*$.

To solve Eq. (12) we write n^* as a linear combination of the eigenvectors of $\mathbf{N}^*$,

$$|n^*\rangle=\sum_\mu a_\mu(\mathbf{x},t)|\eta_\mu\rangle,\tag{16}$$

where the $a_\mu(x,t)$ can depend on space and time. Then Eq. (12) can be transformed into a set of equations

$$\sum_{\mu'}(N_{\mu\mu'}{}^*+R_{\mu\mu'}{}^*)a_{\mu'}=\sum_{\mu'}D_{\mu\mu'}a_{\mu'}\tag{17}$$

for the coefficients $a_\mu(x,t)$. Equation (17) follows from Eq. (12) using Eq. (16) and the orthonormality of the $\{|\eta_\mu\rangle\}$. The operator $N_{\mu\mu'}{}^*$ in Eq. (17) is diagonal, $N_{\mu\mu'}{}^*=\lambda_\mu{}^N\delta_{\mu\mu'}$ although we have not displayed this explicitly in Eq. (17).

Equation (23) could be investigated for a general anisotropic medium with dispersion; indeed these properties are critical in determining the temperature and frequency dependence of the collision operators.[13] On the other hand the temperature deviation and heat current are $\mathbf{q}$-space integral functions of the phonon distribution, and particularly at low temperature arise principally from the isotropic and dispersionless part of the phonon spectrum.

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

The assumption of isotropy serves the purpose of allowing a physical identification of $a_0(\mathbf{x},t)$ and $a_{1x}(\mathbf{x},t)$, $a_{1y}(\mathbf{x},t)$, $a_{1z}(\mathbf{x},t)$ which is pedagogically useful; the general anisotropic case can then be understood in principle. In this assumed isotropic limit, for a single phonon branch (the generalization is apparent and is given in Appendix C) in the long-wavelength limit where $\mathbf{v}(q)=c\mathbf{q}|\mathbf{q}|^{-1}$ it is shown in Appendix A that

$$\epsilon(\mathbf{x},t)=C_v(T_0)\delta T(\mathbf{x},t)=(k_BT/\mu)\langle\eta_0|n^*\rangle=(k_BT/\mu)a_0 \quad (18)$$

and

$$Q_x(\mathbf{x},t)=(k_BThc^2/\lambda_x)\langle\eta_{1x}|n^*\rangle=(k_BThc^2/\lambda_x)a_{1x} \quad (19)$$

where $\epsilon(\mathbf{x},t)=E(\mathbf{x},t)-E_0$ is the deviation in the energy density at $(\mathbf{x},t)$ from the value $E_0=\frac{1}{4}C_vT_0$, the energy density in the phonon system at the average temperature T_0; $Q_x(\mathbf{x},t)$ is the heat current in the x direction at point $(\mathbf{x},t)$ of the crystal. The heat currents in the y and z directions are given by obvious modification of Eq. (19).

Thus the eigenvectors $\{|\eta_0\rangle; |\eta_{1x}\rangle; |\eta_{1y}\rangle, |\eta_{1z}\rangle\}$ play a very special role, being directly related to the experimentally measured quantities δT and $\mathbf{Q}$. In what follows we continue to use this isotropic approximation; however, in the computation of collision rates the true anisotropy or dispersion could be used. That is, the character of the eigenspectrum of $\mathbf{N}^*$, $\{|\eta_\mu\rangle\}$, is related to the translational periodicity of the system, while the scattering rates are related to point-group symmetry.

In order to solve Eq. (23) the structure of the matrices $N_{\mu,\mu'}{}^*$, $R_{\mu\mu'}{}^*$ and $D_{\mu\mu'}$ must be known. These are given in Appendix B. Then the basic equation (17) may be written more concisely by dissecting the "coefficient vector," $\mathbf{a}$, into a_0, $\mathbf{a}_1=(a_{1x},a_{1y},a_{1z})$ and $\mathbf{a}_2=(a_2,a_3,\cdots)$. Then we can write Eq. (17) in the form

$$\left\{\begin{bmatrix}0&0&0\\0&0&0\\0&0&N_{22}{}^*\end{bmatrix}+\begin{bmatrix}0&0&0\\0&R_{11}{}^*&R_{12}{}^*\\0&R_{21}{}^*&R_{22}{}^*\end{bmatrix}-\begin{bmatrix}D_{00}&D_{01}&0\\D_{10}&D_{11}&D_{12}\\0&D_{21}&D_{22}\end{bmatrix}\right\}\begin{Bmatrix}a_0\\\mathbf{a}_1\\\mathbf{a}_2\end{Bmatrix}=0. \quad (20)$$

In this representation the equations may be solved rather simply. First, there is always the separate equation

$$D_{00}a_0+D_{01}\mathbf{a}_1=0, \quad (21)$$

which may be rewritten using Eqs. (A5), (A6), (18) and (19) as

$$\frac{\partial a_0}{\partial t}+\frac{\mu hc^2}{\lambda}\left(\frac{\partial a_{1x}}{\partial x}+\frac{\partial a_{1y}}{\partial y}+\frac{\partial a_{1z}}{\partial z}\right)=0, \quad (22a)$$

or equivalently

$$(\partial\epsilon/\partial t)+\nabla\cdot\mathbf{Q}=C_v[\partial(\delta T)/\partial t]+\nabla\cdot\mathbf{Q}=0. \quad (22b)$$

The energy conservation condition is satisfied as it must be, having been imposed on the collision operators $\mathbf{N}^*$ and $\mathbf{R}^*$.

Proceeding to the remaining rows of Eq. (20)

$$-D_{11}\mathbf{a}_1-D_{10}a_0=-R_{11}{}^*\mathbf{a}_1-(R_{12}{}^*-D_{12})\mathbf{a}_2$$
$$(N_{22}{}^*+R_{22}{}^*-D_{22})\mathbf{a}_2=-(R_{21}{}^*-D_{21})\mathbf{a}_1$$

it is seen that $\mathbf{a}_2$ may be eliminated to yield

$$D_{11}\mathbf{a}_1+D_{10}a_0=[R_{11}{}^*-(R_{12}{}^*-D_{12})(N_{22}{}^*+R_{22}{}^*-D_{22})^{-1}\times(R_{21}{}^*-D_{21})]\mathbf{a}_1. \quad (23)$$

This important equation is the analog to the momentum balance equation. Defining the quantity in brackets as the phonon momentum relaxation operator τ^{-1}, and substituting according to their definitions for the other quantities, Eq. (23) becomes

$$(\partial\mathbf{a}_1/\partial t)+(\mu hc^2/\lambda)\nabla a_0=-(\tau^{-1})_{11}\mathbf{a}_1 \quad (24a)$$

or

$$(\partial\mathbf{Q}/\partial t)+(\mu hc^2/\lambda)\nabla\epsilon=-(\tau^{-1})_{11}\mathbf{Q}. \quad (24b)$$

Under circumstances that R processes become negligible and N processes are infinitely rapid then the right-hand side of Eqs. (23), (24a), (24b) vanishes. The simultaneous equations

$$(\partial\epsilon/\partial t)+\nabla\cdot\mathbf{Q}=0,$$
$$(\partial\mathbf{Q}/\partial t)+(\mu hc^2/\lambda)^2\nabla\epsilon=0,$$

describe a hydrodynamic wave; in fact this wave is the second-sound mode, in the zero-damping limit. In that limit it is a free collective oscillation.

On the other hand one may rearrange Eqs. (23), (24a), or (24b) to examine the response of the driven system when it may be regarded as having an imposed temperature distribution. Recall that a_0 measures the local temperature; thus, in these equations the a_0 term may be used as the driving term (temperature distribution) and the response $\mathbf{a}_1$ (i.e., heat current $\mathbf{Q}$) may be computed by inverting

$$D_{10}a_0=[(R_{11}{}^*-D_{11})-(R_{12}{}^*-D_{12})(N_{22}{}^*+R_{22}{}^*-D_{22})^{-1}\times(R_{21}{}^*-D_{21})]\mathbf{a}_1, \quad (25a)$$

which can be written as

$$-(\mu hc^2/\lambda)^2C_v\nabla T=(\partial\mathbf{Q}/\partial t)+(\tau^{-1})_{11}\mathbf{Q}. \quad (25b)$$

Formally the inverse of (25b) may be written as $\mathbf{Q}=-\kappa\nabla T$ and κ is the thermal-conductivity operator. To place it in an explicit representation consider that the temperature distribution and heat current are Fourier-analyzed in the customary way, in components $\exp[i(\Omega t-\mathbf{k}\cdot\mathbf{r})]$. Then (see Griffin[14]) one may regard κ as $\kappa(\mathbf{k},\Omega)$. In fact the assumed isotropic dispersionless

[14] P. A. Griffin, Phys. Letters 17, 208 (1965).

limit yields from Eqs. (25a), (25b)

$$Q_x(\mathbf{k},\Omega) = -\tfrac{1}{3}C_v c^2 \tau(\mathbf{k},\Omega)\nabla T, \tag{26}$$

where

$$\tau(\mathbf{k},\Omega) = [\langle \eta_{1x}| (\tau)^{-1} |\eta_{1x}\rangle + i\Omega]^{-1} \tag{27}$$

and the $(\mathbf{k},\Omega)$ dependence resides in $D = i(\mathbf{k}\cdot\mathbf{v}-\Omega)$ whose matrix elements may be computed to obtain D_{11}, D_{12}, D_{22}. The task of computing the inverse called for in Eq. (27) is the subject of the subsequent discussion. However, it should be recognized that Eqs. (26) and (27) constitute a set of complete and formally exact macroscopic equations for the pure phonon field. The coupling to elastic dilatation fields is discussed separately in Sec. V.

III. STEADY-STATE LATTICE THERMAL CONDUCTIVITY

If a constant thermal gradient is present, choose this gradient to be in the x direction, then, $\nabla a_0(\mathbf{x},t) \propto (\partial T/\partial x)$ where $\partial T/\partial x$ is a constant and only the x component of $\mathbf{a}_1$ is nonzero. Further, a_{1x} does not depend upon $(\mathbf{x},t)$. Under these conditions Eq. (26) reduces to

$$Q_x = -\tfrac{1}{3}C_v c^2 \tau(0,0)\nabla_x T, \tag{27a}$$

where

$$\tau(0,0) = \langle \eta_{1x}|\, \mathbf{R}^* - \mathbf{R}^*(1-\mathbf{P})(\mathbf{N}^*+\mathbf{R}^*)^{-1} \times (1-\mathbf{P})\mathbf{R}^*|\eta_1\rangle^{-1} \tag{28}$$

and $(1-\mathbf{P}) = (1-\mathbf{P}_0-\mathbf{P}_1)$ is a projection operator which suppresses the components in $|\eta_0\rangle$, $|\eta_{1x}\rangle$, $|\eta_{1y}\rangle$, $|\eta_{1z}\rangle$. There is a misleading simplicity in this result; the important properties of real crystals are contained in $\tau(0,0)$. Essentially all of the extensive work by Peierls, Klemens, Ziman, Herring, Carruthers, and Callaway[7] concern this aspect of the problem. Our concern here will be with the general structure of $\tau(0,0)$ for various possible relative magnitudes of $\mathbf{R}^*$ and $\mathbf{N}^*$.

When the normal processes are very rapid compared with the R processes, $\mathbf{N}^* \gg \mathbf{R}^*$, the second term on the right-hand side of Eq. (28) approaches zero and

$$\tau(0,0) \to \langle 1|\, \mathbf{R}^*|1\rangle^{-1}. \tag{29}$$

This result corresponds to the so-called Ziman limit, in which relaxation rates i.e., thermal resistivities add. This is particularly apparent when $\mathbf{R}^*$ is replaced by a relaxation time approximation, $\mathbf{R}^* \to -\tau_R^{-1}$, and the definition of $\tau(0,0)$ is employed. The result is

$$\tau(0,0) = \left[\int_0^{x_0} \frac{x^4 e^x}{(e^x-1)^2}dx\right]\left[\int_0^{x_0} \tau_R^{-1}\frac{x^4e^x}{(e^x-1)^2}dx\right]^{-1}, \tag{30}$$

where $x_0 = \Theta_D/T$. The distinction between this limit and the more familiar relaxation-time approximation considered next is significant as has been pointed out by Ziman[15] and Callaway.[16] The analysis of recent experiments on LiF by Berman and Brock[17] and Thacher[18] verify this point.

When the R-processes are very rapid compared with the normal processes, $\mathbf{R}^* \gg \mathbf{N}^*$, Eq. (28) takes the form

$$\tau(0,0) \to [R_{11}^* - R_{12}^* R_{22}^{*-1} R_{21}^*]^{-1}. \tag{3 1}$$

This quantity is equal to $(\mathbf{R}^{*-1})_{11}$ as we can show by considering the basic equation, Eq. (20), with $N_{22}^* = 0$. Then under the conditions for steady state we have

$$a_{1x} = (\mathbf{R}^{*-1})_{11} D_{10} a_0, \tag{32}$$

or

$$Q_x = -\tfrac{1}{3}C_v c^2 (\mathbf{R}^{*-1})_{11}\nabla_x T, \tag{33}$$

where $\mathbf{R}^{*-1}$ represents the inverse of the entire $\mathbf{R}^*$ matrix. Hence, in this limit

$$\tau(0,0) = \langle \eta_{1x}|\, \mathbf{R}^{*-1}|\eta_{1x}\rangle. \tag{34}$$

Using the same relaxation-time approximation for $\mathbf{R}^*$ as above, $\mathbf{R}^{*-1} \to -\tau_R$, we find

$$\tau(0,0) = \left[\int_0^{x_0} \frac{x^4 e^x dx}{(e^x-1)^2}\right]^{-1}\left[\int_0^{x_0} \frac{\tau_R x^4 e^x dx}{(e^x-1)^2}\right], \tag{35}$$

the usual relaxation-time approximation.[7] This is to be compared with Eq. (30).

Briefly the difference between the limit $\mathbf{N}^* \gg \mathbf{R}^*$, Eq. (29), and the limit $\mathbf{R}^* \gg \mathbf{N}^*$, Eq. (30), is that in the former case only the matrix element R_{11}^* need be known while in the latter case the complete structure of the $\mathbf{R}^*$ operator is needed for inversion.

The results for steady-state thermal conductivity can be summarized by the formula

$$\kappa = \tfrac{1}{3}C_v c^2 \tau(0,0), \tag{36}$$

where

$$\tau(0,0) = \langle \eta_{1x}|\frac{1}{1+\mathbf{R}^*\mathbf{N}^{*-1}(1-\mathbf{P})}\mathbf{R}^*|\eta_{1x}\rangle^{-1}, \qquad \mathbf{N}^* \gg \mathbf{R}^*, \tag{37a}$$

$$\tau(0,0) = \langle \eta_{1x}|\frac{1}{1+\mathbf{R}^{*-1}\mathbf{N}^*}\mathbf{R}^{*-1}|\eta_{1x}\rangle, \qquad \mathbf{R}^* \gg \mathbf{N}^*. \tag{37b}$$

In practice the principal issues revolve around knowledge of the eigenvector spectrum of the normal process operator. At present this subject is not well developed, although it now seems timely for more detailed consideration; we restrict ourselves to application of this general formalism to the relaxation-time approximation, where it sheds light on the nature of the approximation.

We propose that the following approximate identification of collision operators and relaxation times preserves the important physical features of the thermal conductivity problem:

(*i*) Assume that the space spanned by $\{|\eta_2\rangle, |\eta_3\rangle, \text{etc.}\}$ comprise a single vector denoted by $|2\rangle$ i.e., $\mathbf{a}_2$ has just

[15] R. Berman *et al.*, Proc. Roy. Soc. (London) **A253**, 403 (1959); J. M. Ziman, Ref. 7.

[16] J. C. Callaway and H. C. von Baeyer, Phys. Rev. **120**, 1149 (1960), Appendix.

[17] R. Berman and J. C. F. Brock (to be published).

[18] P. Thacher, thesis, Cornell University, 1965 (unpublished).

one component. Then, the matrix $\langle 2|N^*|2\rangle$ reduces to the number $N_{22}{}^*$ and, since only a_{1x} is nonzero, the matrix $R_{\mu\mu'}{}^*$ is the simple 2×2 matrix

$$\mathbf{R}^*=\begin{bmatrix} R_{11}{}^*, & R_{12}{}^* \\ R_{21}{}^*, & R_{22}{}^* \end{bmatrix}, \tag{38}$$

whose inverse can be constructed algebraically:

$$(\mathbf{R}^{*-1})=\frac{1}{\det(R^*)}\begin{bmatrix} R_{22}{}^*, & -R_{21}{}^* \\ -R_{21}{}^*, & R_{11}{}^* \end{bmatrix}. \tag{39}$$

In the abbreviated space we are considering $\tau(0,0)$ can also be expressed algebraically

$$\tau(0,0)=\left[R_{11}{}^*-R_{12}{}^*\frac{1}{N_{22}{}^*+R_{22}{}^*}R_{21}{}^*\right]^{-1}. \tag{40}$$

(*ii*) The specification of $\tau(0,0)$ in Eq. (40) requires three numbers to define $\mathbf{R}^*$ (since $R_{12}{}^*=R_{21}{}^*$) and one number to specify $\mathbf{N}^*$.

For $\mathbf{N}^*$ we choose $\mathbf{N}^*=1/\tau_N$ a number not dependent on q which may have been computed from some specific conventional model. Then we identify the matrix element $(\mathbf{N}^{*-1})_{22}=\tau_N$.

For $\mathbf{R}^*$ we choose $\mathbf{R}^*=+1/\tau_R$ a function of q. Further we know from the discussion involving the Ziman limit that when $\mathbf{N}^*\to\infty$, $\tau(0,0)\to\langle 1|\mathbf{R}^*|1\rangle^{-1}$. From Eq. (40), when $\mathbf{N}^*\to\infty$, $\tau(0,0)\to(R_{11}{}^*)^{-1}$, hence we make the identification $R_{11}{}^*=\langle 1|\tau_R{}^{-1}|1\rangle$. If further we assume that $R_{22}{}^*\simeq R_{11}{}^*$ then only $R_{12}{}^*=R_{21}{}^*$ is unspecified. However, we have a further condition to be fulfilled by $\tau(0,0)$ in Eq. (40). When $\mathbf{N}^*\to 0$, $\tau(0,0)\to\langle 1|R^{*-1}|1\rangle$. This condition is fulfilled for

$$(R_{12}{}^*)^2=R_{11}{}^*[R_{11}{}^*-(1/(R^{*-1})_{11})]. \tag{41}$$

In summary, with the identifications

$$\begin{aligned} N_{22}{}^* &\to (1/\tau_N), \\ R_{11}{}^* &\to \langle 1|\tau_R(q)^{-1}|1\rangle, \\ R_{22}{}^* &\simeq R_{11}{}^*, \\ (\mathbf{R}^{*-1})_{11} &\to \langle 1|\tau_R(q)|1\rangle, \end{aligned} \tag{42}$$

then Eq. (40) for $\tau(0,0)$ has the proper limiting behavior for both $\mathbf{N}^*\gg\mathbf{R}^*$ and $\mathbf{R}^*\gg\mathbf{N}^*$.

(*iii*) Substituting from Eq. (42) into Eq. (40) for $\tau(0,0)$ leads to

$$\tau(0,0)=\langle 1|\tau_R|1\rangle\left[\frac{\tau_N+\langle 1|\tau_R{}^{-1}|1\rangle^{-1}}{\tau_N+\langle 1|\tau_R|1\rangle}\right]. \tag{43}$$

Defining the variable $s=\tau_N(\langle 1|\tau_R|1\rangle)^{-1}$ we can write the thermal conductivity in the form

$$\kappa=\tfrac{1}{3}C_v c^2\left[\langle 1|\tau_R|1\rangle\frac{s}{1+s}+\langle 1|\tau_R{}^{-1}|1\rangle^{-1}\frac{1}{(1+s)}\right]. \tag{44}$$

It may be of value to use the definition in Eq. (15) to write out the various quantities in terms of familiar integral expressions. Using Eq. (15) and the relations in Appendix A,

$$\langle 1|\tau_R|1\rangle=(2k_B\hbar^2c^2/C_v)\int d^3q\tau_R(q)q_x \times[2k_BT\sinh(\hbar\omega/k_BT)]^{-2},$$

$$\langle 1|\tau_R{}^{-1}|1\rangle=(3k_B\hbar^2c^2/C_v)\int d^3q[1/\tau_R(q)]q_x{}^2 \times[2k_BT\sinh(\hbar\omega/k_BT)]^{-2},$$

where s is given by

$$s=\frac{1}{\langle 1|\tau_R|1\rangle}\frac{k_B}{C_v}\int d^3q\tau_N(q)(\hbar\omega/k_BT)^2 \times[2\sinh(\hbar\omega/k_BT)]^{-2}$$

where $\tau_N(q)$, for example, is the single-phonon relaxation time for normal processes. When the normal processes are negligible $\mathbf{N}^*\to 0$, $\tau_N\to\infty$ and $s\to\infty$. The second term in Eq. (44) goes to zero and the first term dominates. When the normal processes are very rapid $\mathbf{N}^*\to\infty$, $\tau_N\to 0$ and $s\to 0$, the second term in Eq. (44) dominates. We regard the factors $s/(1+s)$ and $1/(1+s)$ as switches which carry the solution from one limiting form (e.g., $s\to 0$, the Ziman limit) to the other. The switches depend upon the parameter s which measures the ratio of the rate of R-process scattering to the rate of normal process scattering.

The Callaway equation[9] may be written in a form similar to Eq. (44) although the algebra of that equation is unnecessarily complicated by having the matrix elements of products of relaxation times instead of the product of matrix elements. Although we have not stressed this point it is apparent that the identification of collision operators with relaxation times is made in a sufficiently arbitrary way that there is no argument in favor of writing $\langle 1|\tau_N{}^{-1}\tau_R|1\rangle$ in place of $\langle 1|\tau_N{}^{-1}|1\rangle \times\langle 1|\tau_R|1\rangle$, etc. In fact Eq. (44) can be "derived" from the Callaway equation if the matrix elements of products of relaxation times are replaced by the products of the matrix elements. We suggest Eq. (44) as a reasonable alternative to the Callaway equation, with computational advantages.

An intuitive understanding of Eq. (44) is given by the following considerations: The heat current carried by the phonon system is proportional to $N-N_0(T(x))$, the displacement in momentum space of the phonon-distribution function. This displacement has the form, where $\mathbf{v}=c(\mathbf{q}/|\mathbf{q}|)$,

$$\Delta n=N-N_0\simeq\tau\mathbf{v}\cdot\nabla T\partial N_0/\partial T \tag{45}$$

where $\tau(\mathbf{q})$ is a relaxation time which measures the average lifetime of momentum in state $\mathbf{q}$. When the normal processes are slow compared to the R processes, this lifetime is simply $\tau_R(q)$ and the heat current

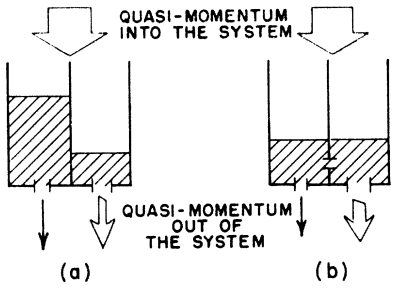

FIG. 1. Schematic analogy of quasimomentum balance in phonon system; (a) represents weak normal processes where various groups of phonons lose momentum individually, while in (b) strong N processes effectively transfer quasimomentum to the strongly scattered state (indicated by the large arrow).

carried by the phonons is proportional to $\langle 1|\tau_R|1\rangle$. [The limit $s\rightarrow\infty$ of Eq. (44).] In the opposite limit, the normal processes are rapid compared to the R processes. Although the R-process mechanism may destroy momentum selectively as a function of $\mathbf{q}$ (e.g., a resonance) the normal processes act as an intermediate to take momentum from states where it is relatively weakly scattered and dump it into the strong scattering states so rapidly that all states lose momentum at the same rate. (The hydraulic analogy in Fig. 1 illustrates this argument.) In these circumstances a single lifetime characterizes the momentum loss from all $\mathbf{q}$ states. This lifetime is $\langle 1|\tau_R^{-1}|1\rangle^{-1}$ [the limit $s\rightarrow 0$ of Eq. (44)].

Finally we point out that measurements of the heat current in a phonon system in the various limits of the rates of normal process scattering and R-process scattering would essentially measure particular matrix elements of R-process scattering. That is, if $\mathbf{N}^*\gg\mathbf{R}^*$ the heat current is a measure of $\langle 1|\mathbf{R}^*|1\rangle=R_{11}^*$; while if $\mathbf{R}^*\gg\mathbf{N}^*$, the heat current is a measure of $(\mathbf{R}^{*-1})_{11}$. Measurements made in the intermediate case depend not only on these two matrix elements, but also on additional matrix elements of the $\mathbf{R}^*$ operator and matrix elements of $\mathbf{N}^*$.

The relationship of these developments to the variational procedure of Ziman is easily seen when the variational procedure is carried out using a linear combination of the eigenvectors of the normal process collision operator as the trial function. The resulting equations for the combination coefficients correspond to our Eq. (20).

IV. $\kappa(k,\Omega)$ AND SECOND SOUND

In the previous section we employed the solution to the Boltzmann equation obtained in Sec. II to the problem of steady-state lattice thermal conductivity. In this section we consider the situation in which δT and $\mathbf{Q}$ can depend upon space and time. The Boltzmann-equation description remains valid for long wavelengths (compared to a lattice constant).

Phenomena in this regime fall into two categories depending upon the composition of τ. These are: (1) $\mathbf{R}^*\gg\mathbf{N}^*$ the momentum loss relaxation time τ_R characterizes the thermalization of the phonon system, $\tau\simeq\tau_R$, (2) $\mathbf{N}^*\gg\mathbf{R}^*$, the momentum conserving relaxation time τ_N characterizes the thermalization of the phonon system, $\tau\simeq\tau_N$. These two circumstances lead to quite different phenomena.

Case 1: $\mathbf{R}^*\gg\mathbf{N}^*$. The basic equations from Sec. II are the statement of energy conservation, Eq. (22b), and the generalized thermal conductivity relation, Eq. (26). In the limit we are presently considering, ($\Omega\tau_R\ll 1$, $\tau_R\ll\tau_N$) the statement of Eq. (26) can be written more conveniently by solving Eq. (20) in a manner similar to that employed in Sec. III in dealing with the steady-state thermal conductivity with $\mathbf{R}^*\gg\mathbf{N}^*$. From Eq. (20) we find

$$\mathbf{a}_1=\langle 1|[1+\mathbf{N}^{*-1}(\mathbf{N}^*-\mathbf{D})]^{-1}\mathbf{R}^{*-1}|1\rangle a_0. \quad (46)$$

Case 2: This was dealt with in Sec. II, Eq. (25):

$$D_{10}a_0=\langle 1|[1+(\mathbf{R}^*-\mathbf{D})\mathbf{N}^{*-1}(1-\mathbf{P})]^{-1}\times(\mathbf{R}^*-\mathbf{D})|1\rangle\mathbf{a}_0. \quad (47)$$

This equation follows from Eq. (25) upon considering the known properties of the operators when operating on $|\eta_1\rangle$. Equations (46) and (47) lead to two alternative expressions for the generalized thermal-conductivity relation. The power-series expansion for the inverse operator in Eq. (46) is a series in $\mathbf{R}^{*-1}(\mathbf{N}^*-\mathbf{D})\simeq((\tau_R/\tau_N)-\tau_R\Omega)$, a factor which is small in the limit corresponding to case 1. The power-series expansion for the inverse operator in Eq. (47) is a series in $((\tau_N/\tau_R)-\tau_N\Omega)$, a factor which is small in the limit corresponding to case 2. The advantage of having the two alternative expressions when dealing with these cases is apparent.

Returning to case 1 we find that Eq. (46) yields

$$\mathbf{a}_1=\langle 1|\mathbf{R}^{*-1}|1\rangle\langle 1|i\mathbf{k}\cdot\mathbf{v}|0\rangle a_0(1+O(\Omega\tau_R)+\cdots, \quad (48)$$

or

$$\mathbf{Q}\simeq-\tfrac{1}{3}C_v c^2\langle 1|\mathbf{R}^{*-1}|1\rangle i\mathbf{k}\delta T. \quad (49)$$

Essentially the result of Eq. (33). We can write this equation in terms of a $\mathbf{k}$- and Ω-dependent thermal conductivity given by

$$\kappa=\tfrac{1}{3}C_v c^2\langle 1|\mathbf{R}^{*-1}|1\rangle(1+O(\Omega\tau_R)+\cdots) \quad (50)$$

which in fact depends on $(\mathbf{k},\Omega)$ only as a small correction.

We remarked earlier that Eqs. (22b) and (25) remained valid even if $\mathbf{a}$ has more general space-time dependence than $\mathbf{a}\propto\exp i(\mathbf{k}\cdot\mathbf{x}-\Omega t)$. Hence, it is possible to write Eq. (46) in the form

$$\mathbf{Q}=-\tfrac{1}{3}C_v c^2\langle 1|\mathbf{R}^{*-1}|1\rangle(1+O(D)+\cdots)\nabla T. \quad (51)$$

Combining this heat-flow equation with the energy-conservation equation yields

$$[\partial(\delta T)/\partial t]=-\chi\nabla^2(\delta T), \quad (52)$$

the Fourier heat law, with $\chi=(\kappa/C_v)$. The solutions are purely diffusive.

For $\mathbf{N}^*\gg\mathbf{R}^*$: The heat current equation, Eq. (47), in the limit $\Omega\tau_N\ll1$, $\Omega\tau_R\gg1$ is to first order

$$\mathbf{a}_1=\frac{\langle1|i\mathbf{k}\cdot\mathbf{v}|0\rangle}{i\Omega+\langle1|\mathbf{R}^*|1\rangle-\langle1|i\mathbf{k}\cdot\mathbf{v}\mathbf{N}^{*-1}(1-\mathbf{P})i\mathbf{k}\cdot\mathbf{v}|1\rangle}a_0, \quad (53)$$

or

$$\mathbf{Q}=-\tfrac{1}{3}C_vc^2[i\Omega+\langle1|\mathbf{R}^*|1\rangle-\langle1|i\mathbf{k}\cdot\mathbf{v}\mathbf{N}^{*-1}(1-\mathbf{P})i\mathbf{k}\cdot\mathbf{v}|1\rangle]^{-1}\nabla T, \quad (54)$$

from which the $\mathbf{k}$- and Ω-dependent thermal conductivity

$$\kappa(\mathbf{k},\Omega)=\tfrac{1}{3}C_vc^2[i\Omega+\langle1|\mathbf{R}^*|1\rangle-\langle1|i\mathbf{k}\cdot\mathbf{v}\mathbf{N}^{*-1}(1-\mathbf{P})i\mathbf{k}\cdot\mathbf{v}|1\rangle]^{-1} \quad (55)$$

can be defined. Under the restrictions of this case $\kappa(\mathbf{k},\Omega)$ is strongly dependent on $\mathbf{k}$ and Ω.

As remarked above we can write Eq. (47) in the form

$$\langle1|\mathbf{v}\cdot\nabla|0\rangle a_0=(\partial\mathbf{a}_1/\partial t)+\langle1|\mathbf{R}^*|1\rangle\mathbf{a}_1-\langle1|\mathbf{v}\cdot\nabla\mathbf{N}^{*-1}\mathbf{v}\cdot\nabla|1\rangle\mathbf{a}_1+\cdots, \quad (56)$$

or

$$\mathbf{Q}+\tau_z\frac{\partial\mathbf{Q}}{\partial t}-\tau_z\langle1|\mathbf{v}\cdot\nabla\mathbf{N}^{*-1}\mathbf{v}\cdot\nabla|1\rangle\mathbf{Q}+\cdots=-\tfrac{1}{3}C_vc^2\tau_z\nabla T, \quad (57)$$

where $\tau_z=\langle1|\mathbf{R}^*|1\rangle^{-1}$ is the relaxation time corresponding to the Ziman limit. This equation along with the energy conservation equation form a set of macroscopic equations for $\mathbf{Q}$ and δT valid in the limit $\Omega\tau_N\ll1$, $\Omega\tau_R\gg1$. This set of equations is closely related to those of Sussmann and Thellung.[10] However, they differ in essential respects, as may be pointed out by changing variables to compare with their notation:

$$\delta T\to T, \quad \mathbf{Q}\to(C_vT_0/3)\mathbf{u},$$

where T_0 is the average temperature, $T=T(\mathbf{x},t)$ is the temperature variation, and $\mathbf{u}$ is the "fluid velocity" of the phonon gas—a definition which we must adopt from Eqs. (19) and (22). The Eq. (22b) and Eq. (57) become

$$(1/T_0)(\partial T/\partial t)+\tfrac{1}{3}\nabla\cdot\mathbf{u}=0 \quad (58)$$

and, if $(\mathbf{N}^*)^{-1}$ is replaced by $\tau_N(|q|)$ and τ_N defined as $\langle1|\tau_N(|q|)|1\rangle$

$$\frac{\partial\mathbf{u}}{\partial t}+\frac{c^2}{T_0}\nabla\mathbf{T}+\left[\frac{1}{\tau_z}-\frac{\tau_Nc^2}{5}(\nabla^2+2\nabla\nabla\cdot)\right]\mathbf{u}=0. \quad (59)$$

Comparing with Sussmann and Thellung; the energy-balance equation (58) does *not* contain a term in τ_N and ∇^2T. This difference is an essential one physically and arises from the linear energy-momentum relation for the phonon gas. The heat current here is linearly proportional to the phonon-gas quasimomentum only, in the isotropic dispersionless limit which describes the leading behavior. The appearance of the R-process relaxation time τ_z in Eq. (57) is an obvious and expected extension of their equations.

Equations (22b) and (57) may be used to examine second sound with damping, Poiseuille flow in a phonon gas, or related problems.

It is possible to discuss "second sound" by employing the macroscopic equations (22b) and (57). This treatment has been given by a number of authors[19]; we do not repeat it here. It is useful to relate our development of the generalized thermal conductivity equation to Griffin's analysis[14] of second sound based on linear response theory. Griffin has shown (using a self-consistency argument analogous to that usually employed in dealing with the dynamic dielectric constant) that the unforced propagation of temperature waves depends upon the singularities of

$$X=\left(1+\frac{k^2\kappa(\mathbf{k},\Omega)}{i\Omega C_v(T_0)}\right)^{-1} \quad (60)$$

or the vanishing of X^{-1}. Explicit expressions for $\kappa(\mathbf{k},\Omega)$ for the limiting cases 1 and 2 are given by Eqs. (50) and (55), respectively.

For case 1, using Eq. (50) the condition $X^{-1}=0$ leads to

$$1-(ik^2c^2/3\Omega)\langle1|R^{*-1}|1\rangle=0 \quad (61)$$

the Fourier transform of Eq. (52). From which $\mathrm{Re}k=\mathrm{Im}k\simeq(1/c)(\Omega/\tau)^{1/2}$, in agreement with the result of Landau and Lifshitz.[20] In this limit thermal waves do not propagate.

For case 2, using Eq. (55) the condition $X^{-1}=0$ leads to

$$1-\frac{k^2c^2}{3\Omega^2}\left[1-i\frac{\langle1|\mathbf{R}^*|1\rangle}{\Omega}-i3\Omega\langle1|\cos^2\theta\mathbf{N}^{*-1}|1\rangle\right]^{-1}=0 \quad (62)$$

for which $\mathrm{Re}(k/\Omega)\simeq\sqrt{3}c^{-1}$ and $\mathrm{Im}(k/\Omega)=-(\sqrt{3}\Delta/2c)$ where $\Delta=[\Omega^{-1}\langle1|\mathbf{R}^*|1\rangle+\Omega\langle|\mathbf{N}^{*-1}|1\rangle]$. Second sound propagates and is weakly damped with a damping coefficient which depends upon τ_R and τ_N. (Compare with our earlier result.[19])

V. COUPLED DILATATION AND PHONON FIELDS

The microscopic treatment of this question has recently been carried out by Martin *et al.*[5] We wish to show the structural relation of our discussion to a set of applicable macroscopic equations, for $N^*\gg R^*$, Case 2 of IV (the Akhiezer limit).

We use a quasi-thermodynamic model,[6] and again consider the isotropic, dispersionless, single longitudinal

[19] J. C. Ward and J. Wilks, Phil. Mag. 42, 314 (1951); 43, 48 (1952); E. W. Prohofsky and J. A. Krumhansl, Phys. Rev. 133, A1403 (1964); R. A. Guyer, and J. A. Krumhansl, Phys. Rev. 133, A1411 (1964); R. N. Gurzhi, Zh. Eksperim. i Teor. Fiz. 19, 490 (1964) [English transl.: Soviet Phys.—JETP 46, 719 (1964)].

[20] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon Press, Inc., New York, 1959), p. 201.

phonon system.[21] Denote the elastic (dilatation) displacement field by $\mathbf{u}$ and the dilatation itself is $\nabla\cdot\mathbf{u}$. In the uncoupled harmonic limit $\mathbf{u}$ will satisfy a wave equation

$$\rho_0(\partial^2\mathbf{u}/\partial t^2)=Y_0\nabla^2\mathbf{u}, \tag{63}$$

with the dispersion relation $\Omega=ck$ and $c=(Y_0/\rho_0)^{1/2}$. The harmonic phonon field may be described using Eqs. (58) and (59), rewritten in terms of the local differential thermal energy $\epsilon_T=C_V\delta T$ and local heat current $\mathbf{Q}$ as

$$(\partial\epsilon_T/\partial t)+\nabla\cdot\mathbf{Q}=0, \tag{64}$$

$$\frac{\partial\mathbf{Q}}{\partial t}+\frac{c^2}{3}\nabla\epsilon_T+\left\{\frac{1}{\tau_z(0,0)}-\frac{\tau_N c^2}{s}(\nabla^2+\nabla\nabla\cdot)\right\}\mathbf{Q}=0. \tag{65}$$

Now assume that it is possible to define a local free-energy per unit volume

$$F=F_{\text{mech}}(\nabla\cdot\mathbf{u})+F_{\text{therm}}(\nabla\cdot\mathbf{u},T), \tag{66}$$

where in fact the thermal part is simply the (quasi-harmonic) free energy of the phonon field, assumed to depend parametrically on the local specific volume through the dilatation $\nabla\cdot\mathbf{u}$. This dependence is expressed in the Grüneisen model through γ, the dependence of the phonon-dispersion relation on the dilatation, i.e.,

$$(\Delta\omega/\omega)=\gamma\nabla\cdot\mathbf{u}. \tag{67}$$

However, generally we have

$$dF=\left[\frac{\partial F_m}{\partial(\nabla\cdot\mathbf{u})}+\frac{\partial F_t}{\partial(\nabla\cdot\mathbf{u})}\right]d(\nabla\cdot\mathbf{u})+\left(\frac{\partial F_t}{\partial T}\right)dT. \tag{68}$$

The isothermal local equilibrium condition is given by

$$[\partial F_m/\partial(\nabla\cdot\mathbf{u})]+[\partial F_t/\partial(\nabla\cdot\mathbf{u})]=0. \tag{69}$$

Taking a harmonic approximation for the mechanical contribution referred to the undeformed zero-temperature state,

$$F_m=(Y_0/2)(\nabla\cdot\mathbf{u})^2+F_3+\cdots, \tag{70}$$

where Y_0^{-1} is the zero-temperature compressibility. Then in (69) the second term may be interpreted as an internal phonon pressure

$$p_t=-[\partial F_t/\partial(\nabla\cdot\mathbf{u})]. \tag{71}$$

The equilibrium condition, neglecting terms in F_3, is

$$Y_0\langle\nabla\cdot\mathbf{u}\rangle_{\text{av}}-p_t=0, \tag{72}$$

and determines the finite-temperature dilatation i.e., thermal expansion. If the phonon free energy does not depend on dilatation i.e., no anharmonic effects, $p_t=0$ and there is neither coupling nor thermal expansion.

Using this model we may then couple Eq. (63) to the phonon system

$$\rho_0(\partial^2\mathbf{u}/\partial t^2)=Y^*\nabla^2\mathbf{u}-\nabla p_t \tag{73}$$

which may be written in terms of the assumed local thermodynamic parameters

$$\rho_0\frac{\partial^2\mathbf{u}}{\partial t^2}=[Y_{0+}O(F_3)]\nabla^2\mathbf{u}-\left(\frac{\partial p_t}{\partial T}\right)\nabla(\delta T). \tag{74}$$

In fact $Y^*=Y^*(T)$ so the first term represents a finite-temperature corrected modulus, while the second term is the "thermoelastic" coupling.[22]

The development of similar coupling terms for the phonons in a medium whose dispersion relations vary with position and time was carried out completely by Kronig[6] for the normal fluid phonon component in liquid helium, with a density fluctuation, $(\delta\rho/\rho_0)=(\nabla\cdot\mathbf{u})$ in the present notation. It is straightforward to apply his analysis to obtain

$$(\partial\epsilon_T/\partial t)+\nabla\cdot\mathbf{Q}=-p_t\partial/\partial t(\nabla\cdot\mathbf{u}) \tag{75}$$

$$\frac{\partial\mathbf{Q}}{\partial t}+\frac{c^2}{3}\nabla\epsilon_T+\left\{\frac{1}{\tau_z(0,0)}-\frac{\tau_N c}{s}(\nabla^2+2\nabla\nabla\cdot)\right\}\mathbf{Q}=c^2p_t\nabla\nabla\cdot\mathbf{u} \tag{76}$$

Thus, coupling terms to the dilatation field appear in the macroscopic phonon field equations.

Taken together Eqs. (74), (75), (76) may describe either "first" or "second" sound propagation and attenuation, and the two are coupled as discussed in greater detail in Refs. 5, 6, and 14.

We may evaluate easily the coupled equations in the Grüneisen approximation and the limit $\tau_R\to\infty$, $\tau_N\to 0$. The resulting coupled dispersion relationship for the Fourier-analyzed waves $\exp[i(\Omega t-\mathbf{k}\cdot\mathbf{x})]$ is

$$\left(\Omega^2-c^2k^2-\frac{3\gamma^2U_T}{\rho_0}k^2\right)\left(\Omega^2-\frac{c^2k^2}{3}\right)-\frac{\gamma^2U_T}{\rho_0}k^2(c^2k^2+\Omega^2)=0 \tag{77}$$

where γ is the Grüneisen constant, U_T the average total local thermal energy. Using the standard thermodynamic relations, the specific heat $C_V=AT^3$ for a phonon system, and the relation

$$(c_p/c_v-1)=Y_0^{-1}T\gamma^2C_V \tag{78}$$

[21] The model used here is intended only to indicate the structure of the coupled problem; it is not as general as that of Woodruff and Enrenreich. The use of local thermodynamic concepts is limited to frequencies for which $\Omega\tau\ll 1$, where τ is of the order of $(\tau_N^{-1}+\tau_R^{-1})^{-1}$.

[22] The term in brackets in Eq. (74) is in fact the isothermal modulus, i.e., $\delta T=0$. The adiabatic modulus is obtained if in (75) $\nabla\cdot\mathbf{Q}=0$, whence δT is obtained from (75) and substituted in (74); in the model used it is found that $c_{\text{ad}}^2=(C_p/C_v)c_{\text{iso}}^2$. However in general for a longitudinal wave neglect of $(\nabla\cdot\mathbf{Q})$ in (75) is only effectively true if in (76) the heat current relaxation rate $[\tau(0,0)^{-1}-(\tau_N c^2/s)(\nabla^2+2\nabla\nabla\cdot)]$ is very large and $\mathbf{Q}$ may be neglected on magnitude grounds. This corresponds to the limit of negligible thermal conductivity.

it may be found that for small γ (weak anharmonicity) there are two roots[23]

$$\Omega^2 \simeq \cdot c^2\left[1+\frac{3}{2}\left(\frac{c_p}{c_v}-1\right)\right]$$
$$\Omega^2 \simeq \frac{c^2}{3}\left[1-\frac{1}{2}\left(\frac{c_p}{c_v}-1\right)\right] \tag{79}$$

which are the first- and second-sound modes, in agreement with Ref. 5. Thus, the essential physical behavior is well described by the Boltzmann description we have developed.

The above assumptions on relaxation rates preclude damping of either first or second sound. To compute the damping of first sound or normal diffusive heat flow the relaxation terms in Eq. (76) must be included. This will be discussed elsewhere. In any case the magnitude of the coupling between dilatation and phonon fields is proportional to $(c_p/c_v-1)^{1/2}$. For a Grüneisen $\gamma=2$, $Y_0^{-1}=10^{-12}$ cm^2 dyn^{-1}, $\Theta_D=10^2$ °K, $T=10$°K then $(c_p/c_v-1)=10^{-4}$.

VI. CONCLUSION

We have developed the solution of a linearized phonon Boltzmann equation in terms of the eigenvector problem for the normal process collision operator for the purpose of investigating steady-state and space-time-dependent phenomena in a phonon gas.

For the pure phonon field, the formal results of this development are summarized in two macroscopic equations relating the temperature deviation and the heat current. The first of these is the usual statement of energy conservation, Eq. (22b); the second is a generalized thermal conductivity equation; $\mathbf{Q}=-\kappa(\mathbf{k},\Omega)i\mathbf{k}\delta T$, for which we obtain an explicit expression for the $\mathbf{k}$- and Ω-dependent thermal conductivity.

By considering the quantity $\kappa(0,0)$ [i.e., $\kappa(\mathbf{k},\Omega)$ for $\mathbf{k},\Omega\rightarrow 0$], we obtain an expression for the steady-state thermal conductivity in terms of matrix elements of the normal process and R-process collision operators. Examination of $\kappa(0,0)$ permits one to understand the interplay of normal processes and R processes in determining the limiting behavior of the thermal conductivity. A model vector space was used for the normal process collision operator in which we derived a simple expression for $\kappa(0,0)$ in terms of relaxation times which represent $\mathbf{N}^*$ and $\mathbf{R}^*$; this expression for $\kappa(0,0)$ is similar to but simpler than the Callaway formula. We propose it as a useful alternative.

The $\mathbf{k}$- and Ω-dependent thermal conductivity and the corresponding macroscopic equations are considered in the regime $\Omega\tau\ll 1$ for the cases $\mathbf{N}^*\ll\mathbf{R}^*$ and $\mathbf{N}^*\gg\mathbf{R}^*$. In the former case we have $\kappa(\mathbf{k},\Omega)\simeq\kappa(0,0)$ and the macroscopic equations lead to the Fourier law of heat diffusion. In the latter case $\kappa(\mathbf{k},\Omega)$ depends strongly upon $\mathbf{k}$ and Ω and a set of macroscopic equations similar to those of Sussmann and Thellung were obtained. We used the expression for $\kappa(\mathbf{k},\Omega)$ to consider the possibility of second sound according to the criterion of Griffin. The expression for $\kappa(\mathbf{k},\Omega)$ when $\mathbf{N}^*\ll\mathbf{R}^*$ leads to strongly damped temperature oscillations; the expression for $\kappa(\mathbf{k},\Omega)$ when $\mathbf{N}^*\gg\mathbf{R}^*$ leads to a weakly damped temperature oscillation, second sound.

Finally, we presented a Grüneisen-like model for the anharmonic coupling between our phonon-field equations and an elastic dilatation field; it was shown that the essential physical aspects of the coupled system may be discussed in this manner without resort to a completely microscopic development. The first- and second-sound modes as well as their coupling and damping may be treated thus.

[23] Here, c is understood to be the isothermal first-sound velocity.

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APPENDIX A

The following distribution functions are known to be unaffected by the normal process collision operator:

$$N(\delta T,0)=[\exp(\hbar\omega/k_B(T+\delta T))-1]^{-1}, \tag{A1}$$
$$N(0,\boldsymbol{\lambda})=[\exp(\hbar\omega+\boldsymbol{\lambda}\cdot\mathbf{q}/k_BT)-1]^{-1}, \tag{A2}$$

which if δT and $\boldsymbol{\lambda}$ are small may be expanded in the deviation from $N(0,0)$

$$|\eta_0\rangle=N(\delta T,0)-N_0(T)=(\delta T/T)[4\sinh^2(x/2)]^{-1}, \tag{A3}$$
$$|\eta_1\rangle=N(0,\lambda)-N_0(T)=\boldsymbol{\lambda}\cdot\mathbf{q}/k_BT_0[4\sinh^2(x/2)]^{-1} \tag{A4}$$

where $x=\hbar\omega/k_BT_0$. We consider these deviations as eigenvectors of the normal process collision operator; and, normalizing to the basis discussed in Ref. 12, define

$$|\eta_0\rangle=\mu[2\sinh(x/2)]^{-1} \tag{A5}$$
$$\left.\begin{matrix}|\eta_{1x}\rangle\\ |\eta_{1y}\rangle\\ |\eta_{1z}\rangle\end{matrix}\right\}=\begin{matrix}\lambda_xq_x\\ \lambda_yq_y\\ \lambda_zq_z\end{matrix}(2k_BT\sinh x/2)^{-1}. \tag{A6}$$

The quantities μ, λ_{1x}, λ_{1y} and λ_{1z} are determined by

$$\langle\eta_\mu|\eta_{\mu'}\rangle=\delta_{\mu,\mu'}.$$

For an isotropic dispersionless medium with phonon velocity we have

$$\mu^2=(k_B/C_v), \quad \lambda^2=(3k_B\hbar^2c^2/C_v). \tag{A7}$$

The moments of the distribution function n^* of interest are

$$\langle\eta_0|n^*\rangle=\frac{V}{(2\pi)^3}\int d\mathbf{q}\mu x(2\sinh x/2)^{-1}\times(2\sinh x/2)n(x), \tag{A8}$$

or

$$\langle\eta_0|n^*\rangle=(\lambda/k_BT)\epsilon_T,$$

where ϵ_T is the energy density measured with respect to the average thermal energy, $\frac{1}{4}C_vT$.

Similarly it follows from the definition of the heat current

$$\mathbf{Q}=V/(2\pi)^3\int\hbar\omega_q\mathbf{v}nd\mathbf{q}$$

that when $\mathbf{v}=c\mathbf{q}(|\mathbf{q}|)^{-1}$, then

$$\langle\eta_{1x}|n^*\rangle=(\lambda_x/k_BT\hbar c^2)Q_x. \tag{A9}$$

These moments may be used to compute the energy density and heat current in the isotropic dispersionless limit.

APPENDIX B

The structure of the collision and drift operators in the vector space of the N-process collision operator can be discussed in the subspaces $|\eta_0\rangle$; $|\eta_{1x}\rangle$, $|\eta_{1y}\rangle$, $|\eta_{1z}\rangle$; $|\delta\rangle$. Here $|\delta\rangle\equiv|\eta_2\rangle$, $|\eta_3\rangle$, etc. is all of the subspace of the collision operator not included among the known zero-eigenvalue solutions.

In this representation the N-process operator is diagonal, and has the structure

$$\mathbf{N}^*=\begin{bmatrix}0&0&0&0&&0&\\0&0&0&0&&&\\0&0&0&0&&0&\\0&0&0&0&&&\\&&&&\lambda_2&&\\0&&0&&&\lambda_3&\\&&&&&&\lambda_4\\&&&&&&&\ddots\end{bmatrix}=\begin{bmatrix}0&0&0\\0&0&0\\0&0&N_{22}^*\end{bmatrix}. \tag{B1}$$

The eigenvalues λ_2, λ_3, $\cdots$, are all positive since the system will equilibrate; thus, while N^* does not have an inverse, N_{22} does (actually, diagonal with elements λ_2^{-1}, λ_3^{-1}, $\cdots$, etc.).

The R-process operator in q space is assumed to conserve energy; this will be the case for anharmonic scattering or elastic scattering by defects. This will not be true for metals where electron scattering of phonons transfers energy out of the phonon system. For nonmetals the structure of $\mathbf{R}^*$ is

$$\mathbf{R}^*=\begin{bmatrix}0&0&0\\0&R_{11}^*&R_{12}^*\\0&R_{21}^*&R_{22}^*\end{bmatrix}, \tag{B2}$$

where again the submatrices may be rectangular or square with dimensions 1, 3, ∞ as appropriate. The diagonal nature of R_{11}^* is apparent for isotropic or cubic systems, since the point-group symmetry operator commutes with R^* and the functions $|\eta_{1x}\rangle$, $|\eta_{1y}\rangle$, $|\eta_{1z}\rangle$ are a basis for one of the (threefold degenerate) irreducible representations; for lower symmetry the structure of R_{11}^* would be more complex. Although R^* does not have an inverse, the matrix in the subspace having $|\eta_0\rangle$ projected out using $1-\mathbf{P}_0=1-|\eta_0\rangle\langle\eta_0|$ i.e.,

$$(1-\mathbf{P}_0)\mathbf{R}^*(1-\mathbf{P}_0)=\begin{bmatrix}R_{11}^*,&R_{12}^*\\R_{21}^*,&R_{22}^*\end{bmatrix} \tag{B3}$$

is nonsingular and does have an inverse.

The drift operator, $(\partial/\partial t)+\mathbf{v}\cdot\nabla$, consists of two parts. The $\partial/\partial t$ is diagonal in $\mathbf{q}$ space. For the general anisotropic case $\mathbf{v}(\mathbf{q})\cdot\nabla\mathbf{x}$ would not have a simple form in the basis being used. For the cubic or isotropic case $\mathbf{v}(\mathbf{q})=c|\mathbf{q}|^{-1}\mathbf{q}$ and belongs to the $|\eta_{1\alpha}\rangle$ irreducible representation. Thus at least in these important cases the structure of D is

$$\mathbf{D}=\begin{bmatrix}\partial/\partial t&\alpha\partial/\partial x&\alpha\partial/\partial y&\alpha\partial/\partial z&0\\\alpha\partial/\partial x&\partial/\partial t&0&0&\\\alpha\partial/\partial y&0&\partial/\partial t&0&D_{12}\\\alpha\partial/\partial z&0&0&\partial/\partial t&\\0&&D_{21}&&D_{22}\end{bmatrix}=\begin{bmatrix}D_{00}&D_{01}&0\\D_{10}&D_{11}&D_{12}\\0&D_{21}&D_{22}\end{bmatrix} \tag{B4}$$

where α is given in terms of the sound velocity c and the normalizing constants λ and μ by

$$\alpha=\mu\hbar c^2/\lambda^2. \tag{B5}$$

Since the problem is linear it may be Fourier-analyzed $a_\mu\exp[i(\Omega t-\mathbf{k}\cdot\mathbf{x})]$; then the matrix elements $\partial/\partial t\rightarrow i\Omega$ and $\partial/\partial x\rightarrow ik_x$. In general $\mathbf{D}$ is expected to have an inverse in the low-frequency limit; we have been unable to define any specific circumstances under which $\mathbf{D}$ becomes singular.

APPENDIX C

The real crystal with three branches of the phonon spectrum must be examined to see whether there are any modifications in fundamental principle from the development and conclusions based on the isotropic single-branch model phonon system.

Consider now that in a monatomic three-dimensional crystal there are three branches characterized by

$$\omega^{(1)}(\mathbf{q}),\quad\omega^{(2)}(\mathbf{q}),\quad\omega^{(3)}(\mathbf{q}). \tag{C1}$$

In general we have three distribution functions $n^{(1)}(\mathbf{q},\mathbf{x},t)$, $n^{(2)}(\mathbf{q},\mathbf{x},t)$, $n^{(3)}(\mathbf{q},\mathbf{x},t)$, obeying

$$\begin{aligned}(\partial n^{(1)}/\partial t)+\mathbf{v}^{(1)}\cdot\nabla n^{(1)}&=\sum_{k=1}^{3}c^{1,k}n^{(k)},\\(\partial n^{(2)}/\partial t)+\mathbf{v}^{(2)}\cdot\nabla n^{(2)}&=\sum_{k=1}^{3}c^{2,k}n^{(k)},\\(\partial n^{(3)}/\partial t)+\mathbf{v}^{(3)}\cdot\nabla n^{(3)}&=\sum_{k=1}^{3}c^{3,k}n^{(k)}.\end{aligned} \tag{C2}$$

It must be understood that the collision operator may scatter intrabranch or interbranch, but that in any case

$$E=\sum_{\mathbf{q}}[n^{(1)}\hbar\omega^{(1)}+n^{(2)}\hbar\omega^{(2)}+n^{(3)}\hbar\omega^{(3)}] \quad \text{(C3)}$$

is conserved for elastic collisions, while for N-processes

$$\Pi=\sum_{\mathbf{q}}[n^{(1)}\hbar\mathbf{q}^{(1)}+n^{(2)}\hbar\mathbf{q}^{(2)}+n^{(3)}\hbar\mathbf{q}^{(3)}] \quad \text{(C4)}$$

is conserved. Thus the two distributions (A1) are zero-eigenvalue eigenfunctions of the N-process collision operator, but with the same T and $\mathfrak{\lambda}$ for each branch. Thus (A5) and (A6) become, defining $x^{(j)}=(\hbar\omega^{(j)}/k_BT)$,

$$|\eta_0{}^{(j)}\rangle=\mu x^{(j)}[2\sinh(x^{(j)}/2)]^{-1}, \quad \text{(C5)}$$

$$|\eta_{1\alpha}{}^{(j)}\rangle=\lambda_\alpha q_\alpha[2k_BT\sinh(x^{(j)}/2)]^{-1} \quad \alpha=x,\ y,\ z \quad \text{(C6)}$$

with the normalization

$$\sum_{j=1}^{3}\langle\eta_\alpha{}^{(j)}|\eta_\beta{}^{(j)}\rangle=\delta_{\alpha,\beta}. \quad \text{(C7)}$$

It is found that, for three isotropic dispersionless branches,

$$\mu^2=k_B[C_v{}^{(1)}+C_v{}^{(2)}+C_v{}^{(3)}]^{-1}, \quad \text{(C8)}$$

$$\lambda^2=3k_B\hbar^2[(C_v{}^{(1)}/c_1{}^2)+(C_v{}^{(2)}/c_2{}^2)+(C_v{}^{(3)}/c_3{}^2)]^{-1}, \quad \text{(C9)}$$

where $C_v{}^{(j)}$ and c_j are the specific heat and sound velocity for the jth branch.

The eigenvalue problem of the $\mathbf{N}^*$ operator is then generalized appropriately as follows:

$$\sum_{k=1}^{3}\mathbf{N}^{*j,k}|\eta_\mu{}^{(k)}\rangle=\lambda_\mu|\eta_\mu{}^{(j)}\rangle, \quad \text{(C10)}$$

$$\sum_j\langle\eta_\mu{}^{(j)}|\eta_{\mu'}{}^{(j)}\rangle=\delta_{\mu,\mu'} \quad \text{(C11)}$$

with the special cases

$$\sum_k\mathbf{R}^{*j,k}|\eta_0{}^{(k)}\rangle=0, \quad \sum_k\mathbf{R}^{*j,k}|\eta_{1\alpha}{}^{(k)}\rangle\neq0,$$

$$\sum_k\mathbf{N}^{*j,k}|\eta_0{}^{(k)}\rangle=0, \quad \sum_k\mathbf{N}^{*j,k}|\eta_{1\alpha}{}^{(k)}\rangle=0.$$

Equations (16) and (17) may then be generalized

$$|n^{(j)*}\rangle=\sum_\mu a_\mu|\eta_\mu{}^{(j)}\rangle, \quad \text{(C12)}$$

and can be placed in the μ,μ' matrix representation of Eq. (17). In that representation the collision operators $\mathbf{N}^*$ and $\mathbf{R}^*$ will have the same structure as given by (B1) and (B2), although the sum over branches must also be taken, e.g.,

$$N_{\mu,\mu'}{}^*=\sum_{j,k}\langle\eta_\mu{}^{(j)}|\mathbf{N}^{*j,k}|\eta_\mu{}^{(k)}\rangle. \quad \text{(C13)}$$

So again,

$$N_{\mu,\mu'}{}^*=\lambda_\mu\delta_{\mu,\mu'},$$

while

$$N_{0,0}{}^*=0, \quad N_{1\alpha,1\alpha}{}^*=0; \quad N_{22}{}^*=\lambda_2, \quad \text{etc.}$$
$$R_{0,0}{}^*=0, \quad R_{0,1\alpha}{}^*=0; \quad R_{0,\mu}{}^*=0;$$

but the matrices $R_{11}{}^*$, $R_{12}{}^*$, $R_{22}{}^*$ as in (C2) are generally nonzero.

On the other hand, the drift operators for the three branches involve the terms $\partial/\partial t$ and $\mathbf{v}^{(j)}\cdot\nabla$. The former is again diagonal in μ,μ' representation while the latter must be evaluated from the expression

$$[\sum_j\langle\eta_\mu{}^{(j)}|\mathbf{v}^{(j)}\cdot|\eta_{\mu'}{}^{(j)}\rangle]\nabla. \quad \text{(C14)}$$

This applies generally, but it is crucial to the structure of Eqs. (21) and (58) that all terms $D_{0,\mu'}=0$ for $\mu'=2,3\cdots$. So considering the special case $\mu=0$, and for three isotropic dispersionless branches,

$$\langle\eta_0{}^{(j)}|=\mu x^{(j)}[2\sinh(x^{(j)}/2)]^{-1}$$

while $\mathbf{v}_j=c_j\mathbf{q}(|\mathbf{q}|)^{-1}$ so that

$$\langle\eta_0{}^{(j)}|v_\alpha{}^{(j)}=\mu\hbar c_j{}^2/\lambda_\alpha\langle\eta_{1\alpha}{}^{(j)}|. \quad \text{(C15)}$$

From symmetry it follows that for each branch

$$\langle\eta_{1\alpha}{}^{(j)}|\eta_0{}^{(j)}\rangle=0,$$

so this gradient term vanishes for $\mu,\mu'=0,0$. For $\mu',\mu=0,1$ it becomes

$$\sum_j\left[\frac{\mu\hbar c_j{}^2}{\lambda_\alpha}\frac{C_v{}^{(j)}}{c_j{}^2}\left(\sum_k\frac{C_v{}^{(k)}}{c_{(k)}{}^2}\right)^{-1}\right],$$

thus,

$$D_{0,1\alpha}=\frac{\mu\hbar}{\lambda_\alpha}\frac{\sum_j C_v{}^{(j)}}{\sum_j C_v{}^{(j)}/c_j{}^2}\frac{\partial}{\partial x_\alpha}, \quad \text{(C16)}$$

which is the generalization of (B5). But we note also that in this isotropic dispersionless case the functional form of $|\eta_{1\alpha}{}^{(j)}\rangle$ for all (j) is the same in q space, differing only by a scaling factor dependent on c_j. Thus the orthogonality $\sum_j\langle\eta_{1\alpha}{}^{(j)}|\eta_\mu{}^{(j)}\rangle=0$; $\mu=2,\ 3,\ \cdots$, must hold for each component (j). From this follows that

$$D_{0,\mu}{}^*=\langle\eta_0{}^{(j)}|\mathbf{v}^{(j)}\cdot|\eta_\mu{}^{(j)}\rangle=0, \quad \text{(C17)}$$

for $\mu=2,\ 3,\ \cdots$. Thus, the structure of $D_{\mu,\mu'}$ is also similar to (B4) except that appropriately weighted velocities must be used, i.e., the specific heat weighting just given.

Some final identifications are needed to obtain the equivalent of Eq. (22b). It may be verified in generalization of (A9) that

$$\langle\eta_{1\alpha}{}^{(j)}|n^*\rangle=(\lambda_\alpha/\hbar k_BTc_j{}^2)Q_\alpha{}^{(j)}, \quad \text{(C18)}$$

i.e., the jth branch component of thermal current in the αth direction, weighted by the inverse square of the sound velocity. But evaluation of the $\langle\eta_0{}^{(j)}|$ moment of the gradient term in each branch of the Boltzmann

equation has just deomonstrated the equality

$$\langle\eta_0^{(j)}|(\mathbf{v}^j)_\alpha=(\mu hc^2/\lambda_\alpha)\langle\eta_{1\alpha}^{(j)}|\,.$$

A typical term of $\langle\eta_{1\alpha}^{(j)}|n^{*(j)}\rangle$ is

$$\langle\eta_0^{(j)}|v_\alpha^{(j)}(\partial/\partial x_\alpha)n^{(j)*}\rangle=(\mu/k_BT)(\partial/\partial x_\alpha)Q_\alpha^{(j)}\,. \quad \text{(C19)}$$

Similarly, as in (A8),

$$\sum_j\langle\eta_0^{(j)}|n^*\rangle=(\mu/k_BT)\epsilon_T\,. \quad \text{(C20)}$$

Thus, taking $\langle\eta_0^{(j)}|$ on the jth Boltzmann equation and summing over j yields

$$(\partial\epsilon_T/\partial t)+\nabla\cdot\mathbf{Q}=0\,. \quad \text{(C21)}$$

We conclude that the presence of several isotropic and dispersionless branches does not modify the essential physical conclusion reached in our main discussion. Dispersion and anisotropy would indeed complicate the details.

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Thermal Conductivity, Second Sound, and Phonon Hydrodynamic Phenomena in Nonmetallic Crystals*

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A variety of phonon-gas phenomena in nonmetals are discussed in a unified manner using a set of macroscopic equations developed from the solution of the linearized phonon Boltzmann equation. This set of macroscopic equations, appropriate for the description of a low-temperature phonon gas, is solved for a cylindrical sample in the limit $\lambda_N\ll R$; $\lambda_N\lambda_R^{\varepsilon}\gg R^2$. Here λ_N is the normal-process mean free path, λ_R^{ε} is the mean free path for momentum-loss scattering calculated in the Ziman limit, and R is the radius of the sample. The solution in this limit exhibits Poiseuille flow of the phonon gas as first discussed by Sussmann and Thellung. An equation for the thermal conductivity which correctly includes this phenomenon is found. Using this equation, the possible outcomes of steady-state thermal-conductivity measurements are discussed in terms of the microscopic scattering rates. Heat-pulse propagation is discussed from a similar point of view. The existence of Poiseuille flow in steady-state thermal-conductivity measurements bears directly on the possibility of observing second sound in solids. A quantitative analysis of available data on LiF suggests that the chemical purity of these samples sets very stringent limits on the observation of either of these effects. The observation of Poiseuille flow in solid He^4 samples by Mezov-Deglin strongly suggests that this material is a prime subject for investigations of second-sound propagation.

I. INTRODUCTION

IN a perfect single crystal of dielectric solid the phonons undergo two distinctly different kinds of scattering processes, normal processes (N-processes) in which quasimomentum is conserved and umklapp processes (U-processes) in which it is not.[1] As the temperature of the solid is varied the relative rate of these scattering processes changes drastically with an attending change in the transport properties involving phonons in the solid. The presence in thermal conductivity of a Ziman limit,[2] and the possibilities of Poiseuille flow[3,4] and the second sound[5–7] in a phonon gas are consequences of these changes. The purpose of this paper is to discuss the entire spectrum of possible low-temperature behavior of a phonon gas from a single unified point of view.

The starting point of the analysis is the system of macroscopic equations derived in the previous paper.[8] These equations describe the time- and space-dependent behavior of a phonon gas; they are set down in Sec. II. Two sets of equations valid in opposite limits (deter-

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