Phonon Boltzmann Equation and Second Sound in Solids*

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It has been suggested that two types of second sound, "drifting" and "driftless," are possible in dielectric crystals. The conditions for the existence of these two types of second sound are obtained, both from a heuristic analysis of the problem and from an exact solution of the complete linearized Boltzmann equation. The exact solution is given in terms of the eigenvalues and eigenvectors of the collision matrix, with the effects of normal processes, umklapp processes, and imperfections included. It is shown that to get drifting second-sound normal-process scattering must dominate so that crystal momentum is approximately conserved; while to get driftless second sound, the scattering must be such that a uniform energy flux will decay exponentially. These conditions for the two types of second sound are not mutually exclusive. It is found that normal-process scattering need not dominate for second sound to exist; but that only when it does dominate, is second sound likely to be observable. The relaxation times for both types of second sound are shown to be the same and equal to the reciprocal of smallest nonzero eigenvalue of the collision matrix. An expression is given for a lower limit on this relaxation time.

I. INTRODUCTION

In order to prevent confusion about the meaning of "second sound" the present discussion is based on the following usage: Second sound will be considered to exist when an accurate description of variations of the local temperature $T(\vec{x}, t)$ requires the use of a damped wave equation of the form

$$\frac{\partial^2 T(\vec{x}, t)}{\partial t^2} + \frac{1}{\tau_{ss}} \frac{\partial T(\vec{x}, t)}{\partial t} - (v_{ss})^2 \nabla^2 T(\vec{x}, t) = 0 \ . \quad (1.1)$$

Here, τ_{ss} and v_{ss} are the relaxation time and the propagation velocity of the second sound.

If "temperature" is replaced by "pressure" or "density" in the above definition, one has the definition of ordinary, or "first sound." Besides the difference in dependent variables, first and second sounds in solids are distinguished by the fact that, except for very special experiments,[1] the damping term $\tau_{ss}^{-1} \partial T/\partial t$ completely dominates the inertial term $\partial^2 T/\partial t^2$ for second sound, while the opposite is true for first sound. Note that the neglect of the first term in (1.1) yields the usual diffusion equation for temperature, while the neglect of the second term yields a wave equation. The solution of (1.1) and its limiting relationship to the solutions of a diffusion equation and of an ordinary wave equation are discussed by Morse and Feshbach.[2] An obvious requirement for second sound to be observable is that the frequency ω, which characterizes the rate of change of the local temperature, be sufficiently high that

$$\omega \tau_{ss} \gtrsim 1 \ . \quad (1.2)$$

When $\omega \tau_{ss} \ll 1$, the solution of (1.1) is indistinguishable from the solution of a diffusion equation.

It is well known that some correction to the diffusion equation is required when the rate of change of the temperature becomes very rapid.[2,3] However, it is neither obvious nor, in general, true that the correction term will take the form of a second derivative with respect to time, as in (1.1). The question of what conditions must prevail for the correction term to have that form, when the medium is a dielectric crystal, is the subject of the present discussion.

A comprehensive review of the theory of second sound in dielectric crystals has been given by Enz,[4] who identifies two types: "drifting" and "driftless." Discussions of second sound based on a Boltzmann equation usually couple a continuity equation for energy balance with a continuity equation for crystal-momentum balance[5-7]; the effect obtained has been called drifting second sound (for the reason mentioned in Sec. III). Discussions of second sound based on many-body theory have led to a different propagation velocity than that obtained by the coupling of the balance equations.[8,9] The effect associated with this different propagation velocity has been called driftless second sound (for lack of a more descriptive name). When the propagation velocity v_{ss} refers specifically to drifting or to driftless second sound, it will be labeled v_{II} or v'_{II}, respectively. Enz[4] has estimated that for solid He^4 the numerical difference between v_{II} and v'_{II} is less than 6%. The significance of the existence of these different types of second sound is investigated here.

The present discussion falls into two parts. First, a heuristic treatment of both drifting and driftless second sounds is given to illustrate the distinction between them with a minimum of mathematical complication. Then, a detailed analysis of the same problem is carried out to show that

the conclusions are rigorously correct and are not just consequences of the simplifying assumptions made in the heuristic analysis.

To clarify the notation used, the elements of the phonon description of transport in lattices are reviewed in Sec. II. The heuristic treatment, which is based on a relaxation-time approximation to the Boltzmann equation, is given in Sec. III. It is shown that: (a) To have drifting second sound, normal-process scattering, which conserves average crystal momentum, must bring about a drifting distribution in a time that is short compared to the time for the umklapp process and imperfection scattering to destroy that distribution. (This requirement is well known.[4–6]) (b) To have driftless second sound, the scattering mechanism must be such that the energy flux decays exponentially. (This requirement is discussed in more detail in Secs. VI and VII.)

In Sec. IV, the properties of the complete linearized phonon Boltzmann equation are discussed in terms of the eigenvalues and eigenvectors of the complete collision matrix; that is, the collision matrix which describes the effects of normal processes, umklapp processes, and imperfections.[10,11] These eigenvectors are used to expand the phonon distribution in a series of eigencomponents. In a spatially uniform system each eigencomponent decays exponentially to zero with a relaxation time that is the reciprocal of the associated eigenvalue. The eigencomponent associated with local equilibrium has an infinite relaxation time.

In Sec. V, an exact solution of the complete linearized Boltzmann equation is obtained for the local temperature $T(\vec{x}, t)$. The conditions under which this solution reduces to a damped wave equation are obtained, and are then analyzed in Sec. VI. It is shown that, even though drifting and driftless second sounds lead to different expressions for the propagation velocity v_{ss}, the relaxation time τ_{ss} is the same in both cases and is equal to the reciprocal of the smallest nonzero eigenvalue of the complete collision matrix. The results are discussed in Sec. VII.

The present discussion makes it clear that the critical requirement for the existence of second sound is that the scattering mechanisms bring about a partially relaxed (or thermalized) intermediate distribution which has a nonzero energy flux in a time that is short compared to the time for the energy flux to be destroyed. It is not necessary that the intermediate distribution be a drifting distribution; that is, it is not necessary that average crystal momentum be approximately conserved.[12] Nevertheless, there is a need for the approximate conservation average crystal momentum, but it is a matter of experimental feasibility, rather than one of theoretical necessity: Since, in practice, second sound is difficult to detect,[1] it is only likely to be detected under the most favorable conditions. For a given material, conditions are most favorable in the temperature range where the relaxation time τ_{ss} is largest. τ_{ss} is largest where normal-process scattering dominates, and that, of course, is the temperature range where average crystal momentum is most nearly a conserved quantity. (That is also where the conditions for drifting second sound are most likely to be satisfied, and where the thermal conductivity has its maximum.)

A convenient formula for estimating the relaxation time is[3,13]

$$\tau_{ss} \approx K/C_0(v_{ss})^2 , \tag{1.3}$$

where K is the thermal conductivity and C_0 is the specific heat per unit volume. It is shown in an Appendix that, when the velocity of driftless second sound v_{II}' is used for v_{ss} in (1.3) the quantity on the right-hand side of (1.3) becomes a lower bound on τ_{ss}.

Many of the equations obtained are strictly correct only for crystals with cubic symmetry. However, one expects similar relationships to hold for crystals with lower symmetry, provided, of course, that they are not too anisotropic. The effect of anisotropy has been discussed by Kwok.[7]

Most of the qualitative results obtained depend only on the applicability of a Boltzmann equation, and do not depend, for example, on whether the excitations described by the Boltzmann equation are bosons or fermions. In particular, many of the results deduced apply to "second spin waves" and to "second sound in metals." That such effects are possible has only been conjectured[14,15]; they have yet to be observed.

II. PRELIMINARIES

The microscopic state of a crystal lattice can be described[16] in terms of the phonon distribution $N_k(\vec{x}, t)$, where $N_k(\vec{x}, t)\, d^3x\, d^3k\, (2\pi)^{-3}$ gives the number of phonons in the volume element d^3x at $\vec{x}$ with wave vectors in the $\vec{k}$-space element d^3k at $\vec{k}$. Here, k stands for $(\vec{k}, s)$ where $\vec{k}$ is the wave vector and s is the polarization index of the mode. The factor of $(2\pi)^{-3}$ reflects the fact that the density of allowed values of $\vec{k}$ in $\vec{k}$ space is $V(2\pi)^{-3}$. Here V refers to the microscopically large, but macroscopically small, volume elements into which the system is divided as an aid in deriving the Boltzmann equation[17] (V can be identified with the element d^3x). One can write

$$N_k(\vec{x}, t) = \langle N_k \rangle_0 + n_k(\vec{x}, t) , \tag{2.1}$$

where $n_k(\vec{x}, t)$ is the deviation of the phonon distribution from $\langle N_k\rangle_0$, its equilibrium value at temperature T_0:

$$\langle N_k\rangle_0 \equiv [\exp(\hbar\omega_k/\kappa T_0) - 1]^{-1} . \quad (2.2)$$

The energy density $u(\vec{x}, t)$, the energy flux $\vec{S}(\vec{x}, t)$, the crystal-momentum density $\vec{J}(\vec{x}, t)$, and the crystal-momentum flux $t^{ij}(\vec{x}, t)$ are related to the distribution $n_k(\vec{x}, t)$ as follows:

$$u(\vec{x}, t) = V^{-1} \sum_k n_k(\vec{x}, t)\, \hbar\omega_k , \quad (2.3a)$$

$$\vec{S}(\vec{x}, t) = V^{-1} \sum_k n_k(\vec{x}, t)\, \hbar\omega_k \vec{v}_k , \quad (2.3b)$$

$$\vec{J}(\vec{x}, t) = V^{-1} \sum_k n_k(\vec{x}, t)\, \hbar\vec{k} , \quad (2.3c)$$

$$t^{ij}(\vec{x}, t) = V^{-1} \sum_k n_k(\vec{x}, t)\, \hbar k^i v_k^j . \quad (2.3d)$$

Here, $\vec{v}_k$ is the group velocity $\partial\omega_k/\partial\vec{k}$, and superscripts designate the components of vectors. The factors of V^{-1} in (2.3a)–(2.3d) allows one to approximate the indicated sums over normal modes by sums over the polarization index and integrals over the first Brillouin zone:

$$V^{-1} \sum_k \to (2\pi)^{-3} \sum_s \int d^3k . \quad (2.4)$$

Any distribution n_k can be written as

$$n_k = \tfrac{1}{2}(n_k + n_{-k}) + \tfrac{1}{2}(n_k - n_{-k}) , \quad (2.5)$$

where $k = (\vec{k}, s)$ and $-k = (-\vec{k}, s)$; the first term on the right-hand side of (2.5) is the *even* part and the second term is the *odd* part of n_k. Since $\omega_k = \omega_{-k}$ and $\langle N_k\rangle_0 = \langle N_{-k}\rangle_0$ are even, and $\vec{v}_k = -\vec{v}_{-k}$ is odd, and since the first Brillouin zone is symmetric about $\vec{k} = 0$, the energy density u and the crystal-momentum flux t^{ij} depend only on the even part of n_k, while energy flux $\vec{S}$ and crystal-momentum density $\vec{J}$ depend only on the odd part.

Note that both u and t^{ij} refer to deviations from an equilibrium value at temperature T_0. In particular, note that the complete energy density is

$$U(\vec{x}, t) = U_0 + u(\vec{x}, t) , \quad (2.6)$$

where $U_0 = V^{-1} \sum_k \langle N_k\rangle_0 \hbar\omega_k$. (2.7)

As is conventional in kinetic theory, the local temperature will be determined by the requirement that the energy density $U(\vec{x}, t)$ and the local temperature $T(\vec{x}, t)$ be related by the same functional relationship that relates U_0 to T_0 in equilibrium. Only small deviations from equilibrium will be considered, so that this requirement becomes

$$U(\vec{x}, t) = U_0 + C_0[T(\vec{x}, t) - T_0] , \quad (2.8)$$

where C_0 is the specific heat per unit volume:

$$C_0 \equiv \frac{dU_0}{dT_0} = V^{-1} \sum_k \frac{d\langle N_k\rangle_0}{dT_0} \hbar\omega_k . \quad (2.9)$$

It follows from (2.6) and (2.8) that

$$u(\vec{x}, t) = C_0[T(\vec{x}, t) - T_0]. \quad (2.10)$$

For future reference, note that the phonon distribution n_k associated with a small uniform change in the temperature is given by the local equilibrium distribution

$$n_k^0(T(\vec{x}, t)) \equiv \frac{d\langle N_k\rangle_0}{dT_0}\,[T(\vec{x}, t) - T_0] , \quad (2.11)$$

where $\dfrac{d\langle N_k\rangle_0}{dT_0} = \dfrac{\hbar\omega_k}{4\kappa T_0^2\,[\sinh(\hbar\omega_k/2\kappa T_0)]^2}$. (2.12)

III. HEURISTIC TREATMENT OF SECOND SOUND

The damped wave equation for second sound is an equation for the space and time dependence of the local temperature. The local temperature is related to the phonon distribution $n_k(\vec{x}, t)$ through Eqs. (2.3a) and (2.10). The time and space dependence of $n_k(\vec{x}, t)$ is determined by the Boltzmann equation.

Any distribution can be expressed as a sum of eigencomponents, as is explained in detail in Sec. IV. The collisions of phonons with each other and with imperfections cause every eigencomponent (except n_k^0) to decay to zero with its own characteristic relaxation time. However, to simplify the discussion here, the following approximate Boltzmann equation, in which the decay to local equilibrium is characterized by a single relaxation time τ, will be used:

$$\frac{\partial n_k(\vec{x}, t)}{\partial t} + \vec{v}_k \cdot \nabla n_k(\vec{x}, t) = -\frac{n_k(\vec{x}, t) - n_k^0(T(\vec{x}, t))}{\tau} . \quad (3.1)$$

$n_k^0(T(\vec{x}, t))$ is the local equilibrium distribution defined by (2.11); the value of $T(\vec{x}, t)$ is determined by the requirement that energy be conserved.

This approximate Boltzmann equation can be expected to be useful if all the eigencomponents important to the problem being considered, except n_k^0, have approximately the same relaxation time. In practice, temperature measurements are averages over some finite, but small, intervals of time Δt [Δt is essentially the reciprocal of the frequency ω introduced in (1.2)]. As a result, quantities which decay to zero with a relaxation time much shorter than Δt will not contribute appreciably to these averages, so that the only eigencomponents important for second sound are those with relaxation times of the order of, or greater than, Δt.

The energy balance equation is important for the discussion of both types of second sound. It is obtained by multiplying either (3.1) or the complete Boltzmann equation (4.1) by $\hbar\omega_k$, summing over all modes, and using (2.3). The result is

$$\frac{\partial}{\partial t} u(\vec{x}, t) + \nabla \cdot \vec{S}(\vec{x}, t) = 0. \quad (3.2)$$

Drifting Approximation

For the drifting approximation to be valid, normal-process scattering must relax a general distribution to a drifting distribution in a time much shorter than the time for umklapp process and imperfection scattering to relax this intermediate distribution to local equilibrium. The drifting distribution is

$$\begin{aligned} N_k^D(\vec{x}, t) &= \langle N_k \rangle_0 + n_k^D(\vec{x}, t) \\ &= (\exp\{[\hbar\omega_k - \hbar\vec{k} \cdot \vec{V}(\vec{x}, t)]/\kappa T(\vec{x}, t)\} - 1)^{-1} \\ &\cong \langle N_k \rangle_0 + n_k^0(T(\vec{x}, t)) \\ &\quad + \frac{d\langle N_k \rangle_0}{dT_0} \frac{T_0}{\omega_k} \vec{k} \cdot \vec{V}(\vec{x}, t), \end{aligned} \quad (3.3)$$

where the approximation indicated by $\cong$ is valid when the deviation from the equilibrium distribution $\langle N_k \rangle_0$ is small. N_k^D is the most probable distribution consistent with the constraint that $U(\vec{x}, t)$ and $\vec{J}(\vec{x}, t)$ not vary.[18] The values of these two quantities determine the value of $T(\vec{x}, t)$ and $\vec{V}(\vec{x}, t)$. The similarity of the distribution N_k^D to the most probable distribution for real boson particles (i.e., bosons for which $\hbar\vec{k}$ is the mechanical momentum) with an average drift velocity $\vec{V}(\vec{x}, t)$ has suggested the use of the word "drifting" for characterizing the distribution N_k^D and the results based on it.

In this approximation, the densities and fluxes are determined by the local values of the temperature $T(\vec{x}, t)$ and drift velocity $\vec{V}(\vec{x}, t)$, as is easily verified by combining (3.3) with Eqs. (2.3). One finds that (2.3a) reduces to (2.10), and that

$$S_D^j(\vec{x}, t) = \sum_i T_0 \left(V^{-1} \sum_k \frac{d\langle N_k \rangle_0}{dT_0} v_k^j \hbar k^i \right) V^i(\vec{x}, t), \quad (3.4a)$$

$$J_D^j(\vec{x}, t) = \sum_i T_0 \left(V^{-1} \sum_k \frac{d\langle N_k \rangle_0}{dT_0} \frac{k^j}{\omega_k} \hbar k^i \right) V^i(\vec{x}, t), \quad (3.4b)$$

$$t_D^{ij}(\vec{x}, t) = \left(V^{-1} \sum_k \frac{d\langle N_k \rangle_0}{dT_0} \hbar k^i v_k^j \right) [T(\vec{x}, t) - T_0]. \quad (3.4c)$$

In a lattice with cubic symmetry the tensor quantities in square brackets in the above are proportional to the unit matrix δ^{ij}.

The crystal-momentum balance equation is obtained by multiplying the Boltzmann equation (3.1) by $\hbar k^i$ and summing over all modes. One obtains

$$\frac{\partial J^i(\vec{x}, t)}{\partial t} + \sum_j \frac{\partial t^{ij}(\vec{x}, t)}{\partial x^j} = -\frac{J^i}{\tau}(\vec{x}, t). \quad (3.5)$$

The term on the right-hand side reflects the fact that average crystal momentum, unlike energy or mechanical momentum, is only approximately conserved, because of umklapp process and imperfection scattering.[19]

A damped wave equation for $T(\vec{x}, t)$ for a lattice with cubic symmetry can be obtained by using (2.10) and (3.4) to combine the energy balance equation (3.2) with the gradient of (3.5). The resulting equation has the form of (1.1) with τ_{ss} and $(v_{ss})^2$ being, respectively, equal to τ and to

$$(v_{II})^2 \equiv \left(V^{-1} \sum_k \frac{d\langle N_k \rangle_0}{dT_0} \hbar\vec{k} \cdot \vec{v}_k \right)^2 \times \left(3C_0 V^{-1} \sum_k \frac{d\langle N_k \rangle_0}{dT_0} \frac{\hbar\vec{k} \cdot \vec{k}}{\omega_k} \right)^{-1}. \quad (3.6)$$

v_{II} is the velocity of drifting second sound for crystals with cubic symmetry. The appropriate value for τ is the relaxation time characterizing the decay of a drifting distribution to a local equilibrium distribution.

Energy Flux and Crystal-Momentum Density

In practice one expects the energy flux $\vec{S}$ to be roughly proportional to the crystal-momentum density $\vec{J}$, at least at low temperatures where the dispersion of the phonon frequency spectrum is unimportant. Such a proportionality holds in the drifting approximation. In general, however, $\vec{S}$ is not proportional to $\vec{J}$. This follows from the fact that Eq. (2.3b) for $\vec{S}$ cannot be reduced to Eq. (2.3c) for $\vec{J}$ by the simple factoring out of some constants. In fact, it is possible for $\vec{S}$ to be zero while $\vec{J}$ is not zero. This is even theoretically possible in the drifting approximation: It would require that the term within the large parentheses in (3.4a) be zero, while that in (3.4b) be nonzero. Now, if the energy flux were zero, the energy balance equation (3.2) would reduce with the aid of (2.10) to the equation $\partial T(\vec{x}, t)/\partial t = 0$, which is certainly not a damped wave equation! Yet, average crystal momentum could, at least in principle, still be approximately conserved. This possibility, although very unlikely in practice, does illustrate the fact that the energy flux, not the average crystal momentum, is the critical quantity for second sound. This, of course, is obvious from the fact that a change in the local temperature requires a change in the energy density, which in turn requires a flux of energy.

The following derivation illustrates how a damped wave equation for $T(\vec{x}, t)$ can be obtained when all that is known about the intermediate distribution is that a nonzero energy flux is associated with it.

Driftless Approximation

For the driftless approximation to be valid, collisions must cause an arbitrary distribution to relax to a distribution of the following form in a time that is short compared to the time for this intermediate distribution to relax to local equilibrium:

$$n_k(\vec{x}, t) = n_k^0(T(\vec{x}, t)) + n_k^{\text{odd}}(\vec{x}, t) \ . \tag{3.7}$$

Here, the even part of n_k is assumed to be a local equilibrium distribution, while no assumption about the form of the odd part is being made. For such a distribution to result, all of the even eigencomponents other than n_k^0 must have significantly shorter relaxation times than the eigencomponents contained in n_k^{odd}. (In Sec. IV it is shown that eigencomponents are either even or odd.)

An expression for the time derivative of the energy flux can be obtained by multiplying (3.1) by $\hbar\omega_k v_k^i$ and summing over all modes:

$$\frac{\partial}{\partial t} S^i(\vec{x}, t) + \sum_j V^{-1} \sum_k \frac{\partial n_k(\vec{x}, t)}{\partial x^j} \hbar\omega_k v_k^i v_k^j = -\frac{S^i(\vec{x}, t)}{\tau} \ . \tag{3.8}$$

By substituting (3.7) into the second term on the left of (3.8), multiplying by τ, and rearranging terms, one can show that

$$\left(\tau\frac{\partial}{\partial t} + 1\right) S^i(\vec{x}, t) = -\sum_j K^{ij} \frac{\partial T(\vec{x}, t)}{\partial x^j}, \tag{3.9}$$

where $$K^{ij} = \tau V^{-1} \sum_k \frac{d\langle N_k\rangle_0}{dT_0} \hbar\omega_k v_k^i v_k^j \ . \tag{3.10}$$

Here K^{ij} is as defined a single relaxation-time approximation to the thermal conductivity. Equation (3.9) has the form of Fourier's law for heat conduction with a correction term $\tau\partial\vec{S}/\partial t$, which is only significant when the flux is rapidly varying. [Eq. (3.9) is equivalent to Eq. (5) of Chester.[3]]

A damped wave equation for $T(\vec{x}, t)$ for a lattice with cubic symmetry, for which $K^{ij} = K\delta^{ij}$, can be obtained by combining the gradient of (3.9) with the energy balance equation (3.2). Using the relationship between $u(\vec{x}, t)$ and $T(\vec{x}, t)$ given by (2.10), one can show that the resulting equation has the form of (1.1) with τ_{ss} and $(v_{ss})^2$ being respectively equal to τ and to

$$(v_{II}')^2 \equiv (C_0 V)^{-1} \sum_k \frac{d\langle N_k\rangle_0}{dT_0} \hbar\omega_k \tfrac{1}{3}\vec{v}_k \circ \vec{v}_k \ . \tag{3.11}$$

v_{II}' is the velocity of driftless second sound for crystals with cubic symmetry.

It follows from (3.9) that an energy flux not driven by a temperature gradient will decay exponentially. That is, if $\nabla T = 0$, then $\vec{S}(t) = \vec{S}(0)\, e^{-t/\tau}$. This means that all of the eigencomponents which can give rise, when excited, to an appreciable energy flux must have approximately the same relaxation time. (The approximate value of these relaxation times is the appropriate value for τ.) This suggests that the validity of the driftless approximation requires that the eigencomponents which give rise, when excited, to a significant flux of energy must have roughly the same relaxation times. That this is indeed the case is verified in Sec. VI.

Approximate Expressions for Velocities of Second Sound

For acoustic modes near the zone center, it is true to the approximation that the frequency spectrum is isotropic that

$$\omega_{\vec{k}s} \simeq v_s|\vec{k}| \quad \text{and} \quad \vec{v}_{\vec{k}s} \simeq v_s \vec{k}/|\vec{k}| \ , \tag{3.12}$$

where v_1 is the velocity for longitudinal (ordinary) sound waves and $v_2 = v_3$ is the velocity for transverse sound waves. At low temperatures, only these modes are appreciably excited. Using the information, one can show for low temperatures that formula (3.6) for drifting second sound reduces to[20]

$$(v_{II})^2 \simeq \frac{1}{3}\left(\sum_{s=1}^{3} v_s^{-3}\right)\left(\sum_{s=1}^{3} v_s^{-5}\right)^{-1}, \tag{3.13a}$$

while formula (3.11) for driftless second sound reduces to[21]

$$(v_{II}')^2 \simeq \frac{1}{3}\left(\sum_{s=1}^{3} v_s^{-1}\right)\left(\sum_{s=1}^{3} v_s^{-3}\right)^{-1} \ . \tag{3.13b}$$

Note that v_{II} and v_{II}' would be the same if there were but a single polarization branch, or if the first-sound velocities were the same for all branches. Because of this, the distinction between drifting and driftless second sound cannot be understood with models possessing such properties.

IV. PROPERTIES OF COLLISION MATRIX

The phonon Boltzmann equation with the collision term linearized in n_k, the deviations from equilibrium, can be written

$$\frac{\partial n_k(\vec{x}, t)}{\partial t} + \vec{v}_k \circ \nabla n_k(\vec{k}, t) = -V^{-1} \sum_l \tilde{\Omega}_{kl} n_l(\vec{x}, t) \ , \tag{4.1}$$

where $l = (\vec{l}, s')$ and $\vec{l}$, like $\vec{k}$, refers to an allowed wave vector in the first Brillouin zone. The collision matrix $\tilde{\Omega}_{kl}$ can be written [13,22]

$$\tilde{\Omega}_{kl} = \tilde{\Gamma}_{kl} + \tilde{\Lambda}_{kl} \ , \tag{4.2}$$

where $\tilde{\Gamma}_{kl}$ is due to anharmonic forces and $\tilde{\Lambda}_{kl}$ is due to randomly distributed lattice imperfections.

The following simple transformation changes $\tilde{\Omega}_{kl}$ into a symmetric matrix[23]:

$$\tilde{\Omega}'_{lk} = \tilde{\Omega}'_{kl} \equiv \tilde{\Omega}_{kl}\left(\frac{\sinh(\hbar\omega_k/2\kappa T)}{\sinh(\hbar\omega_l/2\kappa T)}\right) \ . \tag{4.3}$$

Using (4.3) one can write the Boltzmann equation in the symmetrized form

$$\frac{\partial f_k(\vec{x}, t)}{\partial t} + \vec{v}_k \cdot \nabla f_k(\vec{x}, t) = -V^{-1} \sum_l \tilde{\Omega}'_{kl} f_l(\vec{x}, t), \quad (4.4)$$

where the symmetrized distribution f_k is related to $n_k = N_k - \langle N_k \rangle_0$ by

$$f_k(\vec{x}, t) \equiv n_k(\vec{x}, t) \sinh(\hbar\omega_k / 2\kappa T_0). \quad (4.5)$$

Eigensolutions of Collision Matrix

It is convenient to introduce the eigenvalues $\Omega^{(\alpha)}$ and eigenvectors $\theta_k^{(\alpha)}$ determined by the equation

$$V^{-1} \sum_l \tilde{\Omega}'_{kl} \theta_l^{(\alpha)} = \Omega^{(\alpha)} \theta_k^{(\alpha)}, \quad (4.6)$$

where the superscripts ($\alpha = 0, 1, 2, 3, 4, \ldots$, etc.) in parentheses label the different solutions.

Since $\tilde{\Omega}'_{kl}$ is a real and symmetric matrix,[24] the eigenvectors can be chosen to be real and orthonormal

$$(\theta^{(\alpha)}, \theta^{(\gamma)}) = \delta^{\alpha\gamma}. \quad (4.7)$$

The scalar product is defined by

$$(f, g) \equiv V^{-1} \sum_k f_k g_k = (g, f). \quad (4.8)$$

It follows from the Hermitian character of the Hamiltonian of the lattice that[25]

$$\tilde{\Omega}'_{kl} = \tilde{\Omega}'_{-k-l}, \quad (4.9)$$

where $-l = (-\vec{l}s')$. Using (4.9) and (4.6), one can show that

$$V^{-1} \sum_l \tilde{\Omega}'_{kl} \theta_{-l}^{(\alpha)} = V^{-1} \sum_l \tilde{\Omega}'_{-k-l} \theta_{-l}^{(\alpha)} = \Omega^{(\alpha)} \theta_{-k}^{(\alpha)}. \quad (4.10)$$

That is, if $\theta_k^{(\alpha)}$ is an eigenvector, $\theta_{-k}^{(\alpha)}$ is also an eigenvector with the same eigenvalue. It follows that $\theta_k^{(\alpha)} + \theta_{-k}^{(\alpha)}$ and $\theta_k^{(\alpha)} - \theta_{-k}^{(\alpha)}$ are either eigenvectors with the same eigenvalue or are null vectors. Because of this, all eigenvectors can be chosen so that

$$\theta_k^{(\alpha)} = \pm \theta_{-k}^{(\alpha)}. \quad (4.11a)$$

When the plus (minus) sign is appropriate, the eigenvector will be referred to as even (odd) and will be designated by a roman superscript with (without) bar:

$$\theta_k^{(\bar{\imath})} = \theta_{-k}^{(\bar{\imath})} \quad \text{and} \quad \theta_k^{(i)} = -\theta_{-k}^{(i)}. \quad (4.11b)$$

Greek superscripts will be used when referring to both types of eigenvectors.

There are no negative eigenvalues[26]; that is, for all α, one has

$$\Omega^{(\alpha)} \geq 0. \quad (4.12)$$

Only one eigenvalue is necessarily zero. It will be labeled $\alpha = 0$. The associated normalized eigenvector is[17,24]

$$\theta_k^{(0)} = (4\kappa T_0^2 C_0)^{-1/2} \frac{\hbar\omega_k}{\sinh(\hbar\omega_k / 2\kappa T_0)}, \quad (4.13)$$

where C_0 is defined by (2.9).

Interpretation; Eigencomponents

Any distribution f_k can be expressed in the θ representation as

$$f_k(\vec{x}, t) = \sum_\alpha f^{(\alpha)}(\vec{x}, t) \theta_k^{(\alpha)}, \quad (4.14)$$

where $$f^{(\alpha)}(\vec{x}, t) \equiv (\theta^{(\alpha)}, f(\vec{x}, t)). \quad (4.15)$$

It follows from (4.1) and from the orthogonality and completeness of the eigenvectors that the coefficients $f^{(\alpha)}$ are determined by the coupled set of equations

$$\frac{\partial f^{(\alpha)}(\vec{x}, t)}{\partial t} + \sum_\gamma \langle \alpha | \vec{v} | \gamma \rangle \cdot \nabla f^{(\gamma)}(\vec{x}, t) + \Omega^{(\alpha)} f^{(\alpha)}(\vec{x}, t) = 0, \quad (4.16)$$

where the matrix elements of the group velocity are

$$\langle \alpha | \vec{v} | \gamma \rangle \equiv V^{-1} \sum_k \theta_k^{(\alpha)} \vec{v}_k \theta_k^{(\gamma)} = \langle \gamma | \vec{v} | \alpha \rangle. \quad (4.17)$$

Note that, since $\vec{v}_k = -\vec{v}_{-k}$, matrix elements connecting an even eigenvector with another even eigenvector or an odd eigenvector with another odd eigenvector are zero; that is

$$\langle \bar{a} | \vec{v} | \bar{b} \rangle = \langle i | \vec{v} | j \rangle = 0. \quad (4.18)$$

It follows from (4.5) and (4.14) that any distribution n_k can be written as a sum of eigencomponents:

$$n_k(\vec{x}, t) = \sum_\alpha n_k^{(\alpha)}(\vec{x}, t), \quad (4.19)$$

where

$$n_k^{(\alpha)}(\vec{x}, t) = f^{(\alpha)}(\vec{x}, t) \left(\frac{\theta_k^{(\alpha)}}{\sinh(\hbar\omega_k / 2k T_0)} \right). \quad (4.20)$$

Every eigencomponent $n_k^{(\alpha)}$ is either even or odd depending on whether the associated eigenvalue is even or odd. To the extent that gradients can be ignored, each eigencomponent $n_k^{(\alpha)}$ decays exponentially to zero with a relaxation time equal to $1/\Omega^{(\alpha)}$. To show this, simply set $\nabla f^{(\alpha)} = 0$ in (4.16) and solve for $f^{(\alpha)}(t)$. Since we have $\Omega^{(0)} = 0$, the relaxation time of $n_k^{(0)}$ is infinite.

By using (4.5) and (4.14) in (2.3a), one can show with the aid of (4.13) that

$$u(\vec{x}, t) = (4\kappa T_0^2 C_0)^{1/2} f^{(0)}(\vec{x}, t). \quad (4.21)$$

Referring to Sec. II, one determines from (4.21) that

$$f^{(0)}(\vec{x}, t) = (C_0/4\kappa T_0^2)^{1/2}[T(\vec{x}, t) - T_0], \quad (4.22)$$

and from (4.13) and (4.20), that

$$n_k^{(0)}(\vec{x}, t) = n_k^0(T(\vec{x}, t)), \quad (4.23)$$

where n_k^0 is defined by (2.11). That is, the zeroth eigencomponent is the local equilibrium distribution. Note that once one of the four quantities: energy density, local temperature, zeroth eigencomponent, or $f^{(0)}(x, t)$ is specified, the other three quantities are also determined.

Normal Processes; Drifting Distribution

The part of the collision matrix which describes the effects of anharmonic forces can be written as a sum of two parts,

$$\tilde{\Gamma}_{kl} = \tilde{N}_{kl} + \tilde{U}_{kl}, \quad (4.24)$$

where $\tilde{N}_{kl}$ involves only normal processes while $\tilde{U}_{kl}$ involves only umklapp processes. The eigenvalues $N^{(\alpha)}$ and the orthonormal eigenvectors $\phi_k^{(\alpha)}$ of the symmetrized normal-process collision matrix satisfy the equation[27]

$$V^{-1}\sum_l \tilde{N}^1_{kl}\phi_l^{(\alpha)} = N^{(\alpha)}\phi_k^{(\alpha)}. \quad (4.25)$$

Four solutions of this have eigenvalues which are necessarily zero.[27] They will be labeled $\alpha = 0, 1, 2,$ and 3. The eigenvector associated with local equilibrium is the same as that for the complete collision matrix, $\phi_k^{(0)} = \theta_k^{(0)}$. In addition, there are three eigenvectors associated with a phonon drift; they are

$$\phi_k^{(i)} = \frac{A}{4\kappa T_0}\,\frac{\hbar k^i}{\sinh(\hbar\omega_k/2\kappa T_0)} \quad (i = 1, 2, 3), \quad (4.26)$$

where A is a normalization constant, $k = (\vec{k}, s)$, and the k^i are components of the wave vector $\vec{k} = (k^1, k^2, k^3)$. These eigenvectors are related to the drifting distribution (3.3) as follows [see (4.5), (4.13) and (4.26)]:

$$n_k^D(\vec{x}, t)\sinh(\hbar\omega_k/2\kappa T_0) = (C_0/4\kappa T_0^2)^{1/2}[T(\vec{x}, t) - T_0]\phi_k^{(0)} + (T_0/A)\sum_{i=1,2,3} V^i(\vec{x}, t)\phi_k^{(i)}. \quad (4.27)$$

If normal-process scattering dominates umklapp process and imperfection scattering, the eigenvalues of the complete collision matrix associated with the unperturbed eigenvectors (4.26) are given by the perturbation formula[28]

$$\Omega^{(i)} \cong (\phi^{(i)}, \{\tilde{U}' + \tilde{\Lambda}'\}\phi^{(i)}) = (\phi^{(i)}, \tilde{\Omega}'\phi^{(i)}), \quad (4.28)$$

where the last equality follows from the fact that

$$\sum_l \tilde{N}'_{kl}\phi_l^{(i)} = 0 \text{ for } i = 1, 2, \text{ or } 3.$$

Cubic Symmetry

In considering the dependence of the eigenvectors on the operations of the cubic group, it is convenient to write the eigenvectors (4.26) of $\tilde{N}'_{kl}$ as

$$\phi_k^{(i)} = \phi_{\vec{k}s}^{(i)} = \phi_s^{(i)}(k^1, k^2, k^3), \quad (4.29)$$

where $\vec{k} = (k^1, k^2, k^3)$.

The symmetry of the frequency spectrum $\omega_{\vec{k}s}$ is such that these eigenvectors have the following transformation properties:

$$\begin{aligned}
&\phi_s^{(1)}(k^1, k^2, k^3) = -\phi_s^{(1)}(-k^1, k^2, k^3) \\
&\quad = \phi_s^{(1)}(k^1, -k^2, k^3) = \phi_s^{(1)}(k^1, k^2, -k^3), \\
&\phi_s^{(2)}(k^1, k^2, k^3) = \phi_s^{(1)}(k^2, k^3, k^1), \\
&\phi_s^{(3)}(k^1, k^2, k^3) = \phi_s^{(1)}(k^3, k^1, k^2).
\end{aligned} \quad (4.30)$$

Thus, the $\phi_k^{(i)}$ with $i = 1, 2,$ and 3, transform according to one of the three-dimensional representations of the cubic group. Since the normal process, the umklapp process, and (presumably) the imperfection parts of the collision matrix are all invariant under the above simple rotations and reflections, the eigenvectors $\theta_k^{(i)}$ of the matrix $\tilde{N}'_{kl} + \epsilon(\tilde{U}_{kl} + \Lambda^1_{kl})$ with $\epsilon = 0$, which are obtained from $\phi_k^{(1)}$, $\phi_k^{(2)}$, and $\phi_k^{(3)}$ by varying ϵ from 0 to 1, have the same transformation properties as the $\phi_k^{(i)}$. Also, the eigenvalues $\Omega^{(i)}$ obtained from the degenerate eigenvalues $N^{(1)} = N^{(2)} = N^{(3)} = 0$ by the same variation are degenerate and are, in general, different from zero.[29] That is,

$$\Omega^{(1)} = \Omega^{(2)} = \Omega^{(3)} > 0 \quad \text{(cubic symmetry)}. \quad (4.31)$$

It is important to realize that this conclusion does not depend on the perturbation $\tilde{U}'_{kl} + \tilde{\Lambda}'_{kl}$ being small.[29]

The group velocity $v^i_{\vec{k}s} \equiv \partial\omega_{\vec{k}s}/\partial k^i$ for a crystal with cubic symmetry has transformation properties similar to (4.30). Using these transformation properties and those of the eigenvectors with $i = 1, 2,$ or 3, one can show that

$$\langle 0|v^i|j\rangle \propto \delta^{ij} \quad (i, j = 1, 2, 3), \quad (4.32)$$

and

$$(\theta^{(0)}, v^i\phi^{(j)}) \propto \delta^{ij} \quad (i, j = 1, 2, 3). \quad (4.33)$$

Second-Sound Velocities

By substituting (2.12) into Eq. (3.6) for the velocity of drifting second sound and using the formulas for $\theta_k^{(0)}$ and the $\phi_k^{(i)}$ given above, one can show that for crystals with cubic symmetry

$$(v_{II})^2 = \tfrac{1}{9}\Big[\sum_{i=1}^{3}(\theta^{(0)}, v^i\phi^{(i)})\Big]^2 = \tfrac{1}{3}\sum_{i=1}^{3}[(\theta^{(0)}, v^i\phi^{(i)})]^2, \quad (4.34)$$

where (4.33) has been used. Similarly, Eq. (3.11) for the velocity of driftless second-sound can be written for crystals with cubic symmetry as

$$(v_{II}')^2 = \tfrac{1}{3} V^{-1} \sum_k \theta_k^{(0)} \vec{v}_k \cdot \vec{v}_k \theta_k^{(0)} = \tfrac{1}{3} \langle 0 | \vec{v} \cdot \vec{v} | 0 \rangle , \quad (4.35)$$

where the second equality defines the symbol $\langle 0 | \vec{v} \cdot \vec{v} | 0 \rangle$.

V. RIGOROUS TREATMENT OF SECOND SOUND

In this section, the conditions for local temperature variations to be describable by a damped wave equation are obtained from an exact solution of the complete linearized Boltzmann equation. Use will be made of the fact that, if $f^{(0)}(\vec{x}, t)$ satisfies a damped wave equation, then so does $T(\vec{x}, t)$, because of the proportionality of $f^{(0)}(\vec{x}, t)$ to $T(\vec{x}, t) - T_0$. The results obtained depend on the assumption that the only eigenvalue of the complete collision matrix that is zero is $\Omega^{(0)}$, the one associated with local equilibrium. It is assumed that no eigenvalues other than $\Omega^{(0)}$ are smaller than the triply degenerate eigenvalue $\Omega^{(1)}$ [see (4.31)]. Only crystals with cubic symmetry are considered.

The Fourier space and time transform of the components of the symmetrized phonon density $f_k(\vec{x}, t)$ are defined by

$$\bar{f}^{(\alpha)}(\vec{q}, \omega) = (\theta^{(\alpha)}, \bar{f}(\vec{q}, \omega)) , \quad (5.1)$$

where

$$f_k(\vec{x}, t) = (2\pi)^{-2} \int d^3q \int d\omega \, e^{i(\vec{q}\cdot\vec{x} - \omega t)} \bar{f}_k(\vec{q}, \omega) . \quad (5.2)$$

Only integration along the real axes of the complex planes of ω and $\vec{q} = (q^1, q^2, q^3)$ will be considered. The Fourier space and time transforms of the components of the complete Boltzmann equation in symmetrized form [see (4.1), (4.5), and (4.16)] are

$$-i\omega \bar{f}^{(0)} = -i \sum_j \langle 0 | \vec{q} \cdot \vec{v} | j \rangle \bar{f}^{(j)} , \quad (5.3a)$$

$$(\Omega^{(j)} - i\omega) \bar{f}^{(j)} = -i \langle j | \vec{q} \cdot \vec{v} | 0 \rangle \bar{f}^{(0)} - i \sum_{a=0} \langle j | \vec{q} \cdot \vec{v} | \bar{a} \rangle \bar{f}^{(a)} , \quad (5.3b)$$

and

$$(\Omega^{(\bar{a})} - i\omega) \bar{f}^{(\bar{a})} = -i \sum_j \langle \bar{a} | \vec{q} \cdot \vec{v} | j \rangle \bar{f}^{(j)} \quad (\bar{a} \neq 0) , \quad (5.3c)$$

where the dependence of the $f^{(\alpha)}$ on $\vec{q}$ and ω is left implicit and where the notation of (4.11) for even and odd eigensolutions has been used.

To obtain an exact solution for $\bar{f}^{(0)}$, substitute (5.3c) into (5.3b); this leads to

$$(\Omega^{(j)} - i\omega) \bar{f}^{(j)} = -i \langle j | \vec{q} \cdot \vec{v} | 0 \rangle \bar{f}^{(0)} - \sum_m \langle j | M | m \rangle \bar{f}^{(m)} , \quad (5.4)$$

where by definition

$$\langle j | M | m \rangle \equiv \sum_{a \neq 0} \frac{\langle j | \vec{q} \cdot \vec{v} | \bar{a} \rangle \langle \bar{a} | \vec{q} \cdot \vec{v} | m \rangle}{\Omega^{(\bar{a})} - i\omega} . \quad (5.5)$$

If n is the number of distinct odd eigenvectors, $\langle j | M | m \rangle$ is an n×n matrix. The solution of (5.4) for the odd components $f^{(m)}$ is

$$\bar{f}^{(m)} = -i \sum_j \langle m | (\Omega - i\omega + M)^{-1} | j \rangle \times \langle j | \vec{q} \cdot \vec{v} | 0 \rangle \bar{f}^{(0)} , \quad (5.6)$$

where the reciprocal matrix $\langle m | (\Omega - i\omega - M)^{-1} | j \rangle$ is defined so that

$$\sum_j \langle m | (\Omega - i\omega - M)^{-1} | j \rangle \times [(\Omega^{(j)} - i\omega)\delta_{jn} + \langle j | M | n \rangle] \equiv \delta_{mn} . \quad (5.7)$$

The substitution of (5.6) into (5.3a) yields the following exact equation for $\bar{f}^{(0)}$:

$$i\omega \bar{f}^{(0)} = \sum_{jm} \langle 0 | \vec{q} \cdot \vec{v} | j \rangle \langle j | (\Omega - i\omega + M)^{-1} | m \rangle \times \langle m | \vec{q} \cdot \vec{v} | 0 \rangle \bar{f}^{(0)} . \quad (5.8)$$

It is readily verified that

$$\langle j | (\Omega - i\omega + M)^{-1} | m \rangle = D(j)^{-1} \langle j | R | m \rangle , \quad (5.9)$$

when the elements of the diagonal matrix $D(j)$ are defined by

$$D(j) \equiv \Omega^{(j)} - i\omega + \langle j | M | j \rangle , \quad (5.10)$$

and the reciprocal matrix $\langle j | R | m \rangle$ is defined by

$$\sum_m \langle j | R | m \rangle [\delta_{mn} + \langle m | M | n \rangle_{nd} D(m)^{-1}] \equiv \delta_{jn} . \quad (5.11)$$

The subscript nd in (5.11) indicates that only the nondiagonal elements of $\langle m | M | n \rangle$ are included; the diagonal elements are included in $D(j)$. The reciprocal $\langle j | R | m \rangle$ can be expressed as

$$\langle j | R | m \rangle = \delta_{jm} - \langle j | M | m \rangle_{nd} D(m)^{-1} + \sum_n \langle j | M | n \rangle_{nd} D(n)^{-1} \langle n | M | m \rangle_{nd} D(m)^{-1} + \cdots . \quad (5.12)$$

A sufficient condition for the convergence of this expansion is that[30]

$$\sum_m | \langle j | M | m \rangle_{nd} D(m)^{-1} | < 1 \quad (5.13)$$

for all j. Now, for real values of ω and $\vec{q}$ the real part of $D(m)$ is

$$\mathrm{Re} D(m) = \Omega^{(m)} + \sum_{\bar{a} \neq 0} [\langle m | \vec{q} \cdot \vec{v} | \bar{a} \rangle]^2 \frac{\Omega^{(\bar{a})}}{(\Omega^{(\bar{a})})^2 + \omega^2} , \quad (5.14)$$

so that Re $D(m)$ is always greater than $\Omega^{(m)}$. Since $|D(m)| > \mathrm{Re} D(m)$, the modulus $|D(m)|$ is always greater than Ω. Using this and (5.6), one can reduce condition (5.13) to the requirement that, for all j,

$$\sum_{m(\neq j)} \sum_{\bar{a}\neq 0} \frac{|\langle j|\vec{q}\cdot\vec{v}|\bar{a}\rangle\langle\bar{a}|\vec{q}\cdot\vec{v}|m\rangle|}{\Omega^{(\bar{a})}\Omega^{(m)}} \ll 1. \quad (5.15)$$

To the approximation that (5.15) is satisfied, one has

$$\langle j|R|m\rangle \cong \delta_{jm} . \quad (5.16)$$

With this, Eq. (5.8) becomes

$$i\omega\bar{f}^{(0)} = \sum_j [\langle 0|\vec{q}\cdot\vec{v}|j\rangle]^2 D(j)^{-1}\bar{f}^{(0)} . \quad (5.17)$$

Drifting Approximation

For the drifting approximation to result, two approximations in addition to (5.16) are needed. First, one needs

$$\sum_j \frac{|\langle 0|\vec{q}\cdot\vec{v}|j\rangle|^2}{D(j)} \cong \sum_{j=1}^{3} [\langle 0|\vec{q}\cdot\vec{v}|j\rangle]^2[\Omega^{(1)} - i\omega]^{-1} . \quad (5.18)$$

With $\Omega^{(1)} = \Omega^{(2)} = \Omega^{(3)}$, this approximation is good provided (a) that $D(j) \approx \Omega^{(j)} - i\omega$, which requires that

$$\Omega^{(j)} \gg \sum_{\bar{a}\neq 0} \frac{|\langle j|\vec{q}\cdot\vec{v}|\bar{a}\rangle|^2}{\Omega^{(\bar{a})}} \quad (5.19)$$

for all odd eigensolutions j, and (b) that

$$\sum_{j=1}^{3} |\langle 0|\vec{q}\cdot\vec{v}|j\rangle|^2 \gg \sum_{j\neq 1,2,3} |\langle 0|\vec{q}\cdot\vec{v}|j\rangle|^2 \frac{|\Omega^{(1)} - i\omega|}{|\Omega^{(j)} - i\omega|} . \quad (5.20)$$

Second, it is required that

$$\sum_{j=1}^{3} [\langle 0|\vec{q}\cdot\vec{v}|j\rangle]^2 = |\vec{q}|^2 \frac{1}{3} \sum_{j=1}^{3} [\langle 0|v^j|j\rangle]^2 \cong |\vec{q}|^2 \frac{1}{3} \sum_{j=1}^{3} [(\theta^{(0)}, v^j\phi^{(j)})]^2 . \quad (5.21)$$

The equality in (5.21) follows from (4.32), which is true for crystals with cubic symmetry. The approximation in (5.21) is valid if $\theta_k^{(i)} \simeq \phi_k^{(i)}$ for $i = 1, 2,$ and 3. This, of course, requires that $\tilde{U}'_{kl} + \tilde{\Lambda}'_{kl}$ constitute but a small perturbation to the normal-process collision matrix $\tilde{N}'_{kl}$.

The last term on the right-hand side of (5.21) is the velocity of drifting second sound as given by (4.34). Consequently, with the above approximations Eq. (5.17) becomes

$$-\omega^2\bar{f}^{(0)} - i\omega\Omega^{(1)}\bar{f}^{(0)} + |q|^2(v_{II})^2\bar{f}^{(0)} = 0 . \quad (5.22)$$

Equation (5.22) is the Fourier transform of a damped wave equation for $f^{(0)}(\vec{x}, t)$ with a second-sound velocity of v_{II} and a relaxation time of $1/\Omega^{(1)}$. It then follows immediately from (5.22) and (4.22) that $T(\vec{x}, t)$ satisfies a damped wave equation with $v_{ss} = v_{II}$ and $\tau_{ss} = 1/\Omega^{(1)}$.

Driftless Approximation

For the driftless approximation to result, the following approximation is needed in addition to (5.16):

$$\sum_j [\langle 0|\vec{q}\cdot\vec{v}|j\rangle]^2 D(j)^{-1} \cong \sum_j [\langle 0|\vec{q}\cdot\vec{v}|j\rangle]^2 [\Omega^{(1)} - i\omega]^{-1} . \quad (5.23)$$

In crystals with cubic symmetry this requires (a) that (5.19) be satisfied, and (b) that

$$\sum_j |\langle 0|\vec{q}\cdot\vec{v}|j\rangle|^2 \gg \sum_{j\neq 1,2,3} |\langle 0|\vec{q}\cdot\vec{v}|j\rangle|^2 \frac{|\Omega^{(j)} - \Omega^{(1)}|}{|\Omega^{(j)} - i\omega|} . \quad (5.24)$$

With the aid of properties (4.18) and (4.32), one can verify for crystals with cubic symmetry that

$$\sum_j [\langle 0|\vec{q}\cdot\vec{v}|j\rangle]^2 = \langle 0|(\vec{q}\cdot\vec{v})^2|0\rangle = |\vec{q}|^2 \tfrac{1}{3}\langle 0|\vec{v}\cdot\vec{v}|0\rangle . \quad (5.25)$$

The term on the right-hand side of (5.25) is the velocity of driftless second sound as given by (4.35). Consequently, Eq. (5.17) with approximation (5.23) takes on the form of the Fourier transform of a damped wave equation for $f^{(0)}(\vec{x}, t)$ [see (5.22)] with a second-sound velocity of v'_{II} and with the same relaxation time as drifting second sound, i.e., $1/\Omega^{(1)}$. It follows immediately that $T(\vec{x}, t)$ satisfies a damped wave equation with $v_{ss} = v'_{II}$ and $\tau_{ss} = 1/\Omega^{(1)}$.

VI. IMPLICATIONS OF RIGOROUS TREATMENT

Two of the conditions for local temperature variations to be describable by a damped wave equation are expressed by (5.15) and (5.19). These conditions are common to both the drifting and the driftless approximations. An inspection of them suggests that (5.19) is probably more restrictive than (5.15), and that (5.19) is probably most restrictive when j has the value 1, 2, or 3. This in turn suggests that the essence of these conditions is contained in a requirement of the form

$$|\vec{q}|^2|\langle 1|\vec{V}|\bar{a}\rangle|^2 \ll \Omega^{(1)}\Omega^{(\bar{a})} , \quad (6.1)$$

which must be satisfied for all even eigensolutions except $\bar{a} = 0$. It is always possible to satisfy (6.1) by limiting the size of $|\vec{q}|$. However, the requirement (1.2) that $\omega\tau_{ss} \approx 1$ (or equivalently $\omega \approx \Omega^{(1)}$) imposes an effective lower limit on $|\vec{q}|$. During a time interval of the order of $1/\omega$, a temperature disturbance will have traveled a distance v_{ss}/ω [see Sec. VII], which suggests that

reciprocal wavelengths at least as large as $|\vec{q}| \approx \omega/v_{ss} \approx \Omega^{(1)}/v_{ss}$ are needed for second sound to be observed. With this bound on $|\vec{q}|$, condition (6.1) becomes

$$(|\langle 1|\vec{v}|\bar{a}\rangle|/v_{ss})^2 \ll (\Omega^{(\bar{a})}/\Omega^{(1)}) \quad (\bar{a}\neq 0) \ . \qquad (6.2)$$

This condition will be better satisfied the smaller the degenerate eigenvalue $\Omega^{(1)}$ is relative to the nonzero "even" eigenvalues $\Omega^{(\bar{a})}$. When the requirements for second sound implied in the heuristic treatment are satisfied, $\Omega^{(1)}$ will indeed be smaller than the $\Omega^{(\bar{a})}$. To see this, note that it was assumed in the heuristic treatment that an arbitrary distribution relaxes to an intermediate distribution before relaxing to complete equilibrium. The intermediate distributions considered are the drifting distribution (3.3) and, for the driftless approximation, the distribution (3.7). The even part of both of these is the local equilibrium distribution. For such intermediate distributions to result, the relaxation times $1/\Omega^{(\bar{a})}$ of the *even* eigencomponents other than the local equilibrium eigencomponent must be appreciably less than the relaxation times of the *odd* eigencomponents which remain. From this and from the assumption that $\Omega^{(1)}$ is the smallest eigenvalue for any of the odd eigencomponents (so that $1/\Omega^{(1)}$ is the longest relaxation time), it follows that $1/\Omega^{(1)} \ll 1/\Omega^{(\bar{a})}$ for $a=0$, so that $\Omega^{(1)}$ will indeed be small relative to the $\Omega^{(\bar{a})}$.

Condition (6.2) is also better satisfied the larger the elements $\langle 0|\vec{v}|\bar{a}\rangle$ are relative to the velocity v_{ss}. However, little can be inferred about the magnitudes of the $\langle 0|\vec{v}|\bar{a}\rangle$ without actually solving for the eigenvectors $\theta_k^{(\bar{a})}$, other than, perhaps, that they are not likely to be appreciably larger, or even as large as v_{ss}.

Drifting Second Sound

At this point it is convenient to introduce a third velocity for second sound. This velocity, which will be labeled $\bar{v}_{II}$, is obtained by not making the approximation $\theta_k^{(i)} \cong \phi_k^{(i)}$, which was made in (5.21):

$$(\bar{v}_{II})^2 \equiv \tfrac{1}{3}\sum_{j=1}^{3}[\langle 0|v^j|j\rangle]^2 = \tfrac{1}{3}\sum_{j=1}^{3}\langle 0|\vec{v}|j\rangle\cdot\langle j|\vec{v}|0\rangle \ . \qquad (6.3)$$

This would be the best value for the velocity of second sound if, for some material and some range of temperatures, normal processes did not dominate, but condition (5.20) for drifting second sound was nevertheless better satisfied than condition (5.24) for driftless second sound. Such a situation is certainly possible. Unfortunately, there is no simple formula for estimating $\bar{v}_{II}$ analogous to formulas (3.13) for v_{II} and v'_{II}, since the only vectors whose functional forms are known are $\theta_k^{(0)}$, $\phi_k^{(1)}$, $\phi_k^{(2)}$, and $\phi_k^{(3)}$ [see (4.13) and (4.26)]. It follows from Eqs. (4.35) and (6.3) that

$$(v'_{II})^2 - (\bar{v}_{II})^2 = \tfrac{1}{3}\sum_{j\neq 1,2,3}\langle 0|\vec{v}|j\rangle\cdot\langle j|\vec{v}|0\rangle > 0 \ . \qquad (6.4)$$

Using (6.4) one can reduce the condition for drifting second sound expressed by (5.20) to the requirement that

$$(\bar{v}_{II})^2 \gg |(v'_{II})^2 - (\bar{v}_{II})^2|\,(\Omega^{(1)}/\Omega^{(j)}) \ , \qquad (6.5)$$

which must be satisfied for all eigenvalues with odd eigencomponents except $\Omega^{(1)}$; the frequency dependence of (5.20) has been ignored.[31] In addition to (6.5), the validity of the drifting approximation requires that condition (6.2) be satisfied and that normal processes dominate, so that $\theta_k^{(i)} \cong \phi_k^{(i)}$ and $\bar{v}_{II} \cong v_{II}$.

Condition (6.5) will be better satisfied the smaller the eigenvalue $\Omega^{(1)}$ is relative to the other "odd" eigenvalues $\Omega^{(j)}$. When the requirements for drifting second sound implied in the heuristic treatment are satisfied, $\Omega^{(1)}$ will indeed be smaller than these $\Omega^{(j)}$. To see this, note that for an arbitrary distribution to first relax to a drifting distribution (as was assumed in the heuristic treatment) the relaxation time of the odd eigencomponents in the drifting distribution must be large compared to the relaxation times $1/\Omega^{(j)}$ of the other odd eigencomponents. The odd part of a drifting distribution is formed with the vectors $\phi_k^{(1)}$, $\phi_k^{(2)}$, and $\phi_k^{(3)}$ [see (4.27)], so that (assuming $\theta_k^{(i)} \cong \phi_k^{(i)}$ for $i=1$, 2 and 3) the odd part of the drifting distribution has the relaxation time $1/\Omega^{(1)}$. Thus, one has $1/\Omega^{(1)} \gg 1/\Omega^{(j)}$ or $\Omega^{(1)} \ll \Omega^{(j)}$.

Driftless Second Sound

The validity of the driftless approximation requires that the condition expressed by (5.24) be satisfied, as well as condition (6.2). When the dependence on frequency is ignored,[31] (5.24) reduces to

$$(v'_{II})^2 \gg \tfrac{1}{3}\sum_{j\neq 1,2,3}\langle 0|\vec{v}|j\rangle\cdot\langle j|\vec{v}|0\rangle\,\frac{\Omega^{(j)}-\Omega^{(1)}}{\Omega^{(j)}} \ . \qquad (6.6)$$

This is equivalent to the requirement for driftless second sound obtained in the heuristic treatment; i.e., the requirement that the eigencomponents which give rise, when excited, to a significant flux of energy must all have roughly the same relaxation times. To see this, note that the energy flux is given by [see (2.3b), (4.5), (4.13), (4.14),

(4.17), and (4.18)]

$$\vec{S}(\vec{x}, t) = (4 T_0 C_0)^{1/2} \sum_j f^{(j)}(\vec{x}, t) \langle 0 | \vec{v} | j \rangle , \quad (6.7)$$

where the sum is over only the odd eigenvectors. For a spatially uniform distribution the coefficients $f^{(j)}$ decay exponentially [see (4.16)] so that (6.7) becomes

$$\vec{S}(t) \propto \sum_j f^{(j)}(0) \langle 0 | \vec{v} | j \rangle \exp(-\Omega^{(j)} t) . \quad (6.8)$$

If condition (6.6) is satisfied, it follows for all j except $j = 1$, 2, or 3 that either

$$| \langle 0 | \vec{v} | j \rangle | \ll v'_{II} \quad \text{or} \quad \Omega^{(j)} \approx \Omega^{(1)} .$$

If this is true, then (6.8) reduces to

$$\vec{S}(t) \approx \vec{S}(0) \exp(-\Omega^{(1)} t).$$

Conversely, if $\vec{S}(t)$ decays exponentially, independent of the values of the coefficients $f^{(j)}(0)$ then, for all $j \neq 1$, 2, or 3, one must have either

$$| \langle 0 | \vec{v} | j \rangle | \ll v'_{II} \text{ or } \Omega^{(j)} \approx \Omega^{(1)} .$$

Implicit in this is the reasonable assumption that the matrix elements $\langle 0 | \vec{v} | j \rangle$ with $j = 1$, 2, and 3 are never actually negligible; that is, even though $\bar{v}_{II}$ is always less than v'_{II} [see (6.3) and (6.4)] it is never negligible compared to v'_{II}.

VII. DISCUSSION

The conditions obtained for the existence of second sound in Sec. VI are formulated in terms of the eigenvalues $\Omega^{(\alpha)}$ and eigenvectors $\theta_k^{(\alpha)}$ of the complete collision matrix. (Here, k specifies both the wave vector $\vec{k}$ and the polarization index s of the phonons.) The eigenvectors can be classified as either even or odd according to their dependence on $\vec{k}$. Local equilibrium is associated with eigenvector $\theta_k^{(0)}$, which is even, and which has an eigenvalue that is zero. The energy flux is associated with the odd eigenvectors. There are three odd eigenvectors labeled $\theta_k^{(1)}$, $\theta_k^{(2)}$, and $\theta_k^{(3)}$, which are of special significance. They are obtained from the three drifting eigenvectors of the normal-process collision matrix by a turning on of the perturbations due to umklapp processes and imperfections. The existence of such a connection between the eigenvectors of the complete collision matrix and those of the normal-process collision matrix does not depend on the difference between the two collision matrices being small. In a crystal with cubic symmetry a degenerate eigenvalue, labeled $\Omega^{(1)}$, is associated with these three special eigenvectors. When second sound is possible, $\Omega^{(1)}$ is the reciprocal of the relaxation time τ_{ss} in (1.1).

Expression (6.2) is a condition which must be satisfied for either drifting or driftless second sound to be possible. Roughly speaking, it specifies that the special degenerate eigenvalue $\Omega^{(1)}$ be no larger than the smallest nonzero even eigenvalue. If this were not the case, the intermediate distribution for processes such that $\omega \tau_{ss} \approx 1$ would not be sufficiently relaxed for $T(\vec{x}t)$, as defined in Sec. II, to be reasonably interpreted as a temperature.

Drifting Second Sound

The condition given by the expression (6.5) applies only to drifting second sound. In essence it specifies that the special eigenvalue $\Omega^{(1)}$ be much smaller than all other nonzero eigenvalues, even or odd. One expects that that will indeed be the case when normal processes dominate: The normal-process collision matrix can then be treated as an unperturbed operator to which umklapp process and imperfection scattering acts as a small perturbation, so that $\Omega^{(1)}$ becomes the perturbed value of an eigenvalue which is exactly zero in the unperturbed problem (see Ref. 10 and Sec. IV). Thus, it follows that the dominance of normal processes, which occurred in Sec. VI as a third condition for drifting second sound, is the really essential condition. Expression (6.5) determines when the dominance of the normal processes is sufficient.

The requirement that $\Omega^{(1)}$ be small is equivalent to the requirement for drifting second sound given by other authors.[1,4] To see this, note that $\Omega^{(1)}$ is essentially the reciprocal of τ_R, the relaxation time for "resistive" processes. The reciprocal of the so-called normal process relaxation time τ_N can be thought of as a parameter for characterizing the size of the next larger eigenvalue, i.e., the smallest eigenvalue larger than $\Omega^{(1)}$. Thus, the requirement that $\Omega^{(1)}$ be small is equivalent to $\tau_N \ll \tau_R$. Of course, for drifting second sound to be observable, it is also required that $\omega\tau \gtrsim 1$.

Other Types of Second Sound

Although the dominance of normal processes can be sufficient for (6.2) and (6.5) to be satisfied, there is no reason to believe that their dominance is necessary for (6.2) and (6.5) to be satisfied. Conceivably, the eigenvalue $\Omega^{(1)}$ could be sufficiently less than all other nonzero eigenvalues without normal processes dominating. If such were the case, temperature variations would still be accurately described by a damped wave equation, but the second-sound velocity would be the quantity $\bar{v}_{II}$, defined by (6.3), not the drifting or the driftless velocities v_{II} or v'_{II}. Thus, there is the possibility of yet a third type of second sound.

The condition which distinguishes driftless sec-

ond sound (the second type) from drifting second sound (the first type) is given by expression (6.6). It specifies that all eigenvectors $\theta_k^{(j)}$ for which $\langle 0|\vec{v}|j\rangle \cdot \langle j|\vec{v}|0\rangle$ makes a significant contribution to $\langle 0|\vec{v}\cdot\vec{v}|0\rangle$ must have eigenvalues $\Omega^{(j)}$ of roughly equal size. Since $\langle 0|\vec{v}|j\rangle$ is certainly not likely to be negligible for $j=1$, 2, or 3 and since $\Omega^{(1)}$ is the eigenvalue for $j=1$, 2, and 3, it follows that for driftless second sound to be possible one must have either $\langle 0|\vec{v}|j\rangle \approx 0$ or $\Omega^{(j)} \approx \Omega^{(1)}$ for all j. Here, $\langle 0|\vec{v}|j\rangle$ is the matrix element of the group velocity connecting the local equilibrium eigenvector $\theta_k^{(0)}$ with the odd eigenvector $\theta_k^{(j)}$.

It is difficult to say much of a qualitative nature about the implications of the above condition. It depends strongly on the actual form of the eigenvectors of the collision matrix and on the size of the associated eigenvalues, and virtually nothing is known about such quantities. A study of them could be most useful. A possible direction for such a study has been suggested by Wannier.[11]

If none of the sets of conditions for the existence of second sound discussed here are satisfied for a particular material and temperature range, it does not follow that the applicability of the diffusion equation for heat extends to arbitrarily rapidly varying processes. It means only that the range of applicability of the diffusion equation cannot necessarily be extended by simply adding on a term which changes it to a damped wave equation. Nothing in the present discussion excludes the possibility of there being even more types of second sounds than the three suggested here.

Significance of Other Types of Second Sound

Until methods are developed for obtaining more information about the eigenvalues and eigenvectors of the complete collision matrix, the main significance of driftless second sound and of the type of second sound with the propagation velocity $\bar{v}_{II}$ is that their existence indicates that normal processes need not dominate for second sound to be possible. They need to dominate only if the second sound is to be of the drifting type. What is essential for the existence of second sound is the slow decay of the energy flux; that is, a flux of energy which is not driven by a temperature gradient must decay sufficiently slowly that the decay can be observed experimentally. With drifting second sound, the decay of an undriven energy flux is determined by the rate of decay of the drifting distribution. With driftless second sound, it is determined by the rate of decay of all of the eigencomponents which contribute to the transport of energy [i.e., eigencomponents j for which $\langle 0|v|j\rangle \neq 0$. See Eq. (6.7)].

The fact that the conservation of average crystal momentum is not a necessary requirement for the existence of second sound in a phonon system indicates that, when investigating the possibility of second sound in other systems, one should consider *all* mechanisms which can lead to a slow decay of the energy flux. The possibility suggested for second sound in metals is an example of a mechanism which has nothing to do with crystal-momentum conservation but, nevertheless, can lead to a slow decay of the energy flux and, thus, to the possibility of second sound.

Since many-body theory has predicted a second-sound velocity v_{II}' different from the velocity v_{II} predicted by previous derivations based on a Boltzmann equation, a question has existed concerning the relationship of the different theoretical velocities to the velocity of observed second sound. The present work facilitates the answering of that question, as it predicts both v_{II} and v_{II}' from an analysis of the same linearized Boltzmann equation. For the reason mentioned in Sec. I, second sound is only likely to be observed (at least at present) when normal processes dominate. Thus, the drifting approximation (with the propagation velocity v_{II}) should certainly apply to any observed second sound. The interesting question is: Is it possible that the driftless approximation (with the propagation velocity v_{II}') also applies? In general, the answer is no, for the following reason.

For the driftless approximation to be valid, one must have either $\langle 0|\vec{v}|j\rangle \approx 0$ or $\Omega^{(j)} \approx \Omega^{(1)}$ for all j. When normal processes dominate, $\Omega^{(1)}$ is much smaller than all other nonzero eigenvalues, so that for drifting and driftless second sound to be possible at the same time, one must have $\langle 0|\vec{v}|j\rangle \approx 0$ except when j refers to one of the three special odd eigenvectors. If this were the case, the eigenvector expansion of the quantity $\theta_k^{(0)}\vec{v}_k$ would involve only the three special eigenvectors. Furthermore, when normal processes dominate, the three special eigenvectors reduce to the drifting eigenvectors given by (4.26). Now, to the extent that dispersion and anisotropy can be ignored, one can prove the following[32]: If $\theta_k^{(0)}\vec{v}_k$ could be expanded in terms of the three drifting eigenvectors only, the velocity of first sound would be the same for all polarizations, and conversely. However, in real materials the velocity of first sound is, in general, considerably lower for the transverse polarizations than it is for longitudinal polarization. As a result, when normal processes dominate, the driftless approximation is, in general, not applicable.

The above argument, of course, does not exclude the possibility of the conditions for both drifting and driftless second sound being satisfied

at the same time.[33] The existence, at least in theory, of such a possibility suggests that the different types of second sound should be thought of not as distinct "modes" of heat propagation, but rather as simply different approximation schemes which lead to the same phenomena.

Some Limitations

It should be emphasized that, since the present work is based on a linearized Boltzmann equation, the applicability of the results obtained (or to be more precise, of the present derivation of the results) is limited to systems to which the linearized Boltzmann equation is applicable. Two important limitations on its applicability should be mentioned. First, the deviation of the phonon distribution from an equilibrium distribution must be small. Otherwise, one is not justified in linearizing with respect to that deviation. Second, lattice disturbances involving very long-wavelength normal modes cannot be described, since the phonons described by the Boltzmann equation are considered to be localized, and localization imposes an uncertainty relation type of restriction on the wavelengths ($\Delta k\ \Delta x > 1$, where $\lambda = 2\pi/k$). In particular, if heat pulses are being considered the length characteristic of the localization of the phonons must be less than the mean free path of the heat pulses ($\Delta x \ll$ mean free path).

Second-Sound Experiments

Most experiments with second sound have been done with thermal pulses.[1] In such experiments a short-duration heat pulse is introduced into a sample at one location and the response is observed at another. Solutions of the damped wave equation corresponding to such an experimental setup are discussed by Morse and Feshbach.[34] They indicate that an attenuated pulse propagates away from the initial disturbance with a velocity v_{ss} and is followed by a diffusive-type wave. The existence of the initial pulse is the result of the addition of the second time derivative term to the diffusion equation, so that its existence can be considered as evidence of second sound. The solution also indicates that the second-sound pulse, which has the shape of the initial pulse, decays as $\exp(-t/2\tau_{ss})$. Consequently, second-sound pulses have an effective mean free path of $2v_{ss}\tau_{ss}$. This can be estimated with the approximate formula $2K/C_0 v_{ss}$, which follows immediately from (1.3); v_{ss} can be estimated from (3.13).

Ackermann and Guyer[1] have estimated the mean free path for solid He^4 and solid He^3. ($2v_{ss}\tau_{ss}$ is equivalent to their mean free path λ_U.) They have also estimated the mean free path for normal processes, so that they have a complete check on the conditions for drifting second sound. Their discussion of the experimental results for solid He^4 and solid He^3 strongly suggest that the second sound has indeed been observed in these materials. Experimenters have also looked for second sound in other dielectrics.[35,36] In the case of the experiments of von Gutfeld and Nethercot it appears that their failure to observe second sound was the result of the very short mean free path of second sound in their samples.[36] These authors did, however, observe some rather interesting pulses which traveled with the energy velocity for first sound. But, because of the large energy inputs which apparently were used, it is likely that the description of these first-sound pulses is outside the range of validity of the linearized Boltzmann equation.

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APPENDIX: LOWER BOUND ON τ_{SS}

According to the kinetic theory of lattice heat conduction, the energy flux is[37]

$$\vec{S} = V^{-1} \sum_k \hat{n}_k \hbar\omega_k \vec{v}_k \ , \tag{A1}$$

where the phonon density $\hat{n}_k$ is the solution of

$$\frac{d\langle N_k\rangle_0}{dT_0}\ \vec{v}_k \cdot \nabla T = -\ V^{-1} \sum_l \tilde{\Omega}_{kl} \hat{n}_l \ . \tag{A2}$$

If one defines a vector $\hat{f}_k = (\hat{f}_k^1, \hat{f}_k^2, \hat{f}_k^3)$ by the equation

$$\hat{n}_k = -\sum_i \frac{\hat{f}_k^i}{\sinh(\hbar\omega_k/2\kappa T)}\ \frac{\partial T}{\partial x^i} \ , \tag{A3}$$

then Eqs. (A1) and (A2) can be rewritten with the aid of (2.12), (4.3), (4.13), and the definition of the thermal conductivity K^{ij} as

$$K^{ij} = (4\kappa T_0^2 C_0)^{1/2} V^{-1} \sum_k \hat{f}_k^j\ \theta_k^{(0)}\ v_k^i \tag{A4}$$

and $$(C_0/4\kappa T_0^2)^{1/2}\ \theta_k^{(0)}\ v_k^i = V^{-1} \sum_l \tilde{\Omega}'_{kl} \hat{f}_l^i \ . \tag{A5}$$

Equations (A4) and (A5) can be solved by expanding $\hat{f}_k$ in the θ representation by solving (A5) for the eigencomponents of $\hat{f}_k$, and then substituting into (A4). The result is

$$K^{ij} = C_0 \sum_m \langle 0|v^i|m\rangle\langle m|v^j|0\rangle / \Omega^{(m)} \ , \tag{A6}$$

where only the odd eigenvectors are summed over. For crystals with cubic symmetry for which $\Omega^{(1)} = \Omega^{(2)} = \Omega^{(3)}$ is the smallest eigenvalue with odd eigenvectors, one has

$$K = \tfrac{1}{3}\ \mathrm{Tr} K^{ij} < C_0\, \tfrac{1}{3} \sum_{im} [\langle 0|v^i|m\rangle]^2 / \Omega^{(1)}$$

$$= C_0 \tfrac{1}{3} \langle 0 | \vec{v} \cdot \vec{v} | 0 \rangle / \Omega^{(1)} \quad , \tag{A7}$$

where Eq. (4.18) and the completeness of the $\theta_k^{(\alpha)}$ have been used. Using Eq. (4.35) for the velocity of driftless second sound, one obtains

$$K < C_0 (v_{II}')^2 / \Omega^{(1)} \quad . \tag{A8}$$

With $\tau_{ss} = 1/\Omega^{(1)}$ this can be rewritten as a lower bound on the relaxation time:

$$\tau_{ss} > K / C_0 (v_{II}')^2 \quad . \tag{A9}$$

If condition (6.6) for driftless second sound is satisfied, the right-hand side of (A9) will not only be a lower bound on τ_{ss}, it will also give a good approximation to τ_{ss}. Such an approximation for τ_{ss} [see (1.3)] can also be obtained from the requirement that a damped wave equation for $T(\vec{x}, t)$ reduce to the usual diffusion equation when slowly varying processes are considered.

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[1]For reviews articles about experimental investigations of second sound in dielectrics see, C. C. Ackerman and R. A. Guyer, Ann. Phys. (N.Y.) 50, 128 (1968); R. J. von Gutfeld, in *Physical Acoustics*, edited by W. P. Mason (Academic, New York, 1968), Vol. V, pp. 233–291.

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[10]J. A. Krumhansl [Proc. Roy. Soc. (London) 85, 921 (1965)] and R. A. Guyer and J. A. Krumhansl [Phys. Rev. 148, 766 (1966); 148, 778 (1966)] have used the eigensolutions of the normal-process part of the collision matrix to discuss second sound.

[11]G. H. Wannier [Bull. Am. Phys. Soc. 14, 303 (1969)] indicates that the eigenvalue spectrum may have both a continuous and a discrete part. The situation could be the same as that for gases [see, G. H. Wannier, *Statistical Physics* (Wiley, New York, 1966), p. 413]. In the present discussion the mathematical complications caused by a continuous spectrum will be avoided by not taking the limit $V \to \infty$. (It is this limit which caused the difficulty: The number of wave vectors $\vec{k}$ equals the number of unit cells in the volume element V, so that taking the limit $V \to \infty$ changes $\vec{k}$ from a discrete to a continuous parameter and the collision matrix from a finite matrix with a discrete eigenvalue spectrum to an integral operator which may have a continuous spectrum.) Nevertheless, even with $V < \infty$, some eigenvalues may be very close to others, so that any approximation requiring that eigenvalues be widely separated in value should be made with caution. The appropriate finite value for V is the volume of the microscopically large but macroscopically small volume element used in the derivation of the Boltzmann equation (see Ref. 17 below). Strictly speaking, the limit $V \to \infty$ is an approximation.

[12]This means that the crystal-momentum density $\vec{J}$ and crystal-momentum flux t^{ij} defined by (2.3) need not even satisfy a modified continuity equation such as (3.5).

[13]Compare this with Eq. (4.35) of Enz; Ref. 4.

[14]Y. V. Gulayev, Zh. Eksperim. i Teor. Fiz. Pis'ma Redaktslyu 2, 3 (1965) [Soviet Phys. JETP Letters 2, 1 (1965)]; R. N. Gurzhi, Fiz. Tverd. Tela 7, 3515 (1965) [Soviet Phys. Solid State 7, 2838 (1966)].

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[16]The notation has been chosen to be consistent with that of R. J. Hardy, J. Math. Phys. 6, 1749 (1965).

[17]See, e.g., G. Leibfried, in *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1955), Vol. VII, part 1, pp. 313–315.

[18]For an example of a derivation of such a most probable distribution, see D. ter Haar, *Elements of Statistical Mechanics* (Rinehart, New York, 1954), Chap. IV.

[19]If one derives a crystal-momentum balance equation, not from (3.1), but from (4.1) with umklapp processes and imperfections ignored, one obtains $\partial J^i/\partial t + \sum_j \partial t^{ij}/\partial x^j = 0$, instead of (3.5).

[20]This is the second-sound velocity given by R. B. Dingle [Proc. Roy. Soc. (London) A65, 1044 (1952), Eq. (3.3)] and J. A. Sussmann and A. Thellung [Proc. Phys. Soc. (London) 81, 1122 (1963), Eq. (14)].

[21]This is the second-sound velocity given by Griffin in Ref. 8 and by Enz in Ref. 4.

[22]Explicit expressions relating $\tilde{\Gamma}_{kl}$ and $\tilde{\Lambda}_{kl}$ to the anharmonic force constants, etc., are given by Eqs. (3.38) and (4.17) of Ref. 16. Also, see Eqs. (1.4), (1.6), and (1.15) in the same reference.

[23]This transformation has been used before by both Krumhansl (Ref. 12) and Hardy (Ref. 16).

[24]See the explicit formulas for the parts of the collision matrix referred to in Ref. 22.

[25]See Eqs. (1.5), (1.8), (3.38), and (4.17) and Ref. 16, pp. 1757–1758.

[26]See Ref. 16, Sec. 6, and Leibfried, Ref. 14, pp. 307–309.

[27]For a more complete discussion of these eigenvectors and eigenvalues, see Ref. 10.

[28]Using the familiar variational principle of elementary quantum mechanics, one can show that the $\simeq$ sign in (4.28) is a $\leq$ sign provided that $\Omega^{(1)} = \Omega^{(2)} = \Omega^{(3)}$ are indeed the smallest eigenvalues with odd eigenvectors.

[29]V. Heine, *Group Theory in Quantum Mechanics* (Pergamon, London, 1960), pp. 44–46.

[30]R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience, New York, 1953), p. 19, footnote.

[31]If the frequency dependence in conditions (5.20) and (5.24) were included in (6.5) and (6.6), the former would become more restrictive as ω increases, while the lat-

ter would become less restrictive. It is interesting to note that Enz (Ref. 9) obtained v'_{II} by considering high frequencies.

[32]To verify this, carry out the eigenvector expansion, substitute in the explicit expression for the eigenvectors given by Eqs. (4.13) and (4.26), let $\omega_{\vec{k}s} = v_s |\vec{k}|$ and $\vec{v}_{ks} = v_s \hat{k}$ (where the v_s are the first-sound velocities), and rearrange terms.

[33]Note that when anisotropy is allowed for, one can have $v_{II} = v'_{II}$ without all of the first-sound velocities being the same. If $v_{II} = v'_{II}$ and if normal processes dominate, the conditions for driftless and for drifting second sound will both be satisfied. Obviously, the essential condition for drifting second sound will be satisfied. That the conditions for driftless second sound will also be satisfied follows from Eq. (6.4) and $\bar{v}_{II} = v_{II} = v'_{II}$. Also, note that when the propagation velocities are equal, the different types of second sound are experimentally indistinguishable.

[34]Morse and Feshbach (Ref. 2) use a first-sound velocity c in forming their correction to the diffusion equation, as they are primarily interested in investigating how an upper bound on the propagation velocity affects diffusion. The present discussion shows that under certain conditions a better value for their c would be the velocity of second sound v_{ss}.

[35]T. F. McNelly, S. J. Rogers, D. J. Channin, R. J. Rollefson, W. M. Goubau, G. E. Schmidt, J. A. Krumhansl, and B. O. Pohl, Phys. Rev. Letters 24, 100 (1970).

[36]R. J. von Gutfeld and A. H. Nethercot, Jr., Phys. Rev. Letters 17, 868 (1966). In their Table II, von Gutfeld and Nethercot give a mean free path of 2.4×10^{-2} cm at 37 °K for their sample. Their heat pulse generator and their detector appear to have been separated by at least 5×10^{-1} cm, which is approximately 20 mean free paths.

[37]See Ref. 16, pp. 1752–1753.

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COMMENTS AND ADDENDA

The Comments and Addenda section is for short communications which are not of such urgency as to justify publication in Physical Review Letters and are not appropriate for regular Articles. It includes only the following types of communications: (1) comments on papers previously published in The Physical Review or Physical Review Letters; (2) addenda to papers previously published in The Physical Review or Physical Review Letters, in which the additional information can be presented without the need for writing a complete article. Manuscripts intended for this section may be accompanied by a brief abstract for information-retrieval purposes. Accepted manuscripts will follow the same publication schedule as articles in this journal, and galleys will be sent to authors.

Comments on Random Walk and Diffusion as Models for Exciton Migration*

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It has been shown that exciton diffusion cannot explain the time dependence of host-sensitized energy transfer in doped organic crystals. It is claimed in a recent publication that formulating exciton migration as a random-walk problem eliminates any discrepancies in the observed and predicted time dependences of the energy transfer. In this paper we show that the two models for exciton migration give exactly the same theoretical predictions, and the anomalous time dependence remains unexplained.

This note is a comment on a recent paper by Rosenstock[1] in which it is claimed that random-walk and diffusion models for energy migration give different theoretical predictions for the time dependence of fluorescence intensities.

We recently demonstrated that studying the complete time evolution of the fluorescence intensities of sensitizers and activators is an important tech-