

Correlation Function Calculation of Thermal Conductivity

WILLIAM C. SCHIEVE

U. S. Naval Radiological Defense Laboratory, San Francisco, California

AND

ROBERT L. PETERSON*

Case Institute of Technology, Cleveland, Ohio

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Recent theories of transport in fluids express the thermal conductivity in terms of correlation functions of the thermal flux. It is shown here that such an expression for the thermal conductivity reduces to that conventionally obtained by use of the Boltzmann transport equation for phonon scattering in crystals, if the rate of change of phonon occupation numbers due to scattering may be characterized by a relaxation time per mode of vibration. The elastic scattering of phonons by randomly arranged scatterers in anisotropic crystals is also discussed. We show that a new relaxation mechanism can, in certain cases, simply characterize the thermal conductivity.

RECENT theories of transport in fluids express the thermal conductivity in terms of correlation functions.^{1,2} It appears that these theories are sufficiently general to be valid for phonon transport in anisotropic solids. In this note we show that the quantum-mechanical expression due to McLennan² gives the same results as the calculation utilizing the Boltzmann transport equation, provided the scattering mechanisms may be characterized by a relaxation time per vibrational mode. In addition it is assumed that for both methods the canonical density matrix and the thermal flux operator are those for the harmonic (unperturbed) lattice.

We also discuss the elastic scattering of phonons in an anisotropic crystal. We note that for scattering of phonons by randomly arranged point defects, having a mass or near neighbor binding force different from the normal, thermal conductivity is governed by relaxation times connecting modes of equal energy and opposite wave vector.

The formula for the thermal conductivity tensor which we take as our starting point is²

$$\kappa_{ij} = V(kT^2)^{-1} \int_{-\infty}^0 dt \langle s_i(0) s_j(t) \rangle, \quad i, j = 1, 2, 3. \quad (1)$$

Alternative expressions to Eq. (1) for κ_{ij} , and other transport coefficients^{1,3,4} include an additional integration over the temperature. However, Verboven⁵ has shown that these expressions reduce essentially to Eq. (1). Here V is the volume of the crystal, k is

Boltzmann's constant, T is the absolute temperature, and

$$\langle s_i(0) s_j(t) \rangle \equiv \text{Tr}[\rho s_i(0) s_j(t)]$$

is the time correlation function of the components of thermal flux. Also, ρ is the canonical density matrix and $\mathbf{s}(t)$ is the Heisenberg representation of the flux defined by

$$\mathbf{s}(t) = \exp(i\hbar^{-1}Ht)\mathbf{s}(0) \exp(-i\hbar^{-1}Ht).$$

The Hamiltonian H is that for the system not including the surroundings. It may be divided into two parts, H^0 for the harmonic system, and H' responsible for the scattering of the phonons. Physically, Eq. (1) establishes a connection between the thermal conductivity describing the irreversible transport of energy and the dissipation of an equilibrium fluctuation in the energy flux.

The correlation function of Eq. (1) in general is not real and does not satisfy the principle of microscopic reversibility.⁶ A way to avoid this difficulty is simply to assert that the correlation function is to be symmetrized, but this does not seem to be a natural consequence of the quantum mechanical theory. However, for the choice of equilibrium density matrix and thermal flux operator usually made, the correlation function of Eq. (1) is, in fact, real and time reversible.

Our aim here is to compare the results of the correlation function calculation with the results of the Boltzmann transport equation calculation for phonon transport. Since in the latter, one chooses the canonical density matrix and flux to be that for the harmonic lattice,^{7,8}

$$\rho = \exp(-\beta H^0) [\text{Tr} \exp(-\beta H^0)]^{-1}, \quad (2)$$

$$\mathbf{s} = V^{-1} \sum_{\mathbf{k}, s} \hbar \omega(\mathbf{k}, s) \mathbf{v}(\mathbf{k}, s) N(\mathbf{k}, s), \quad (3)$$

⁶ S. R. DeGroot, *Thermodynamics of Irreversible Processes* (Interscience Publishers, Inc., New York, 1952).

⁷ P. Carruthers, *Revs. Modern Phys.* **33**, 92 (1961).

⁸ P. G. Klemens, *Solid-State Physics* (Academic Press Inc., New York, 1958), Vol. 7, p. 1.

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¹ H. Mori, *J. Phys. Soc. Japan* **11**, 1029 (1956); *Phys. Rev.* **112**, 1829 (1958).

² J. A. McLennan, Jr., *Phys. Rev.* **115**, 1405 (1959); *Phys. Fluids* **3**, 493 (1960).

³ R. Kubo, M. Yokota, and S. Nakajima, *J. Phys. Soc. Japan* **12**, 1203 (1957).

⁴ R. Kubo, *Lectures in Theoretical Physics* (Interscience Publishers, Inc., New York, 1959), Vol. I, Chap. 4, p. 120.

⁵ E. Verboven, *Physica* **26**, 1091 (1960).

we make the same choice here. In Eqs. (2) and (3) $\beta = (kT)^{-1}$, and \mathbf{k} is the wave vector of the phonon of polarization s ; $\hbar\omega(\mathbf{k},s)$, $\mathbf{v}(\mathbf{k},s)$, and $N(\mathbf{k},s)$ are the energy and group velocity and number operator, respectively, of the phonon in mode (\mathbf{k},s) . The Hamiltonian for the unperturbed lattice is

$$H^0 = \sum_{\mathbf{k},s} \hbar\omega(\mathbf{k},s) [N(\mathbf{k},s) + \frac{1}{2}].$$

Thus, $\mathbf{s}(0)$ and ρ commute ensuring the reality and time reversibility of the correlation function. The symmetrized form of Eq. (1) then also reduces to the same result for these choices. Further, only diagonal matrix elements of ρ , $\mathbf{s}(0)$, and $\mathbf{s}(t)$ are now needed.

From Eq. (3) the time-dependent flux per mode can be written

$$s_j(\mathbf{k},s;t) = V^{-1} \hbar\omega(\mathbf{k},s) v_j(\mathbf{k},s) N(\mathbf{k},s;t).$$

Here $N(\mathbf{k},s;t)$ is the Heisenberg representation of the number operator governed by the equation of motion

$$dN(\mathbf{k},s;t)/dt = i\hbar^{-1} [H, N(\mathbf{k},s;t)]. \quad (4)$$

The diagonal elements of the left-hand side of Eq. (4) give the time rate of change of the phonon occupation numbers due to the scattering by the perturbation H' . This is just the collision term of the Boltzmann transport equation.^{7,8} If this equation can be solved even approximately the solutions appearing in the two formulations of the thermal conductivity will be the same.

Suppose there is a solution to Eq. (4) that has the form of a relaxation time per mode,

$$\langle m | N(\mathbf{k},s;t) | m \rangle = \exp[t/\tau(\mathbf{k},s)] \langle m | N(\mathbf{k},s) | m \rangle.$$

Then

$$\langle s_i(0) s_j(t) \rangle = \sum_{\mathbf{k},s} \langle s_i s_j(\mathbf{k},s) \rangle \exp[t/\tau(\mathbf{k},s)]. \quad (5)$$

The time-independent correlation function $\langle s_i s_j(\mathbf{k},s) \rangle$ can be written

$$\begin{aligned} \langle s_i s_j(\mathbf{k},s) \rangle &= \sum_{\mathbf{k}',s'} \hbar^2 \omega(\mathbf{k}',s') \omega(\mathbf{k},s) v_i(\mathbf{k}',s') v_j(\mathbf{k},s) \\ &\quad \times \langle N(\mathbf{k}',s') N(\mathbf{k},s) \rangle \\ &\quad + \hbar^2 \omega^2(\mathbf{k},s) v_i(\mathbf{k},s) v_j(\mathbf{k},s) \langle N^2(\mathbf{k},s) \rangle \\ &\quad + \hbar^2 \omega(-\mathbf{k},s) \omega(\mathbf{k},s) v_i(-\mathbf{k},s) v_j(\mathbf{k},s) \\ &\quad \times \langle N(-\mathbf{k},s) N(\mathbf{k},s) \rangle. \quad (6) \end{aligned}$$

The summation is over all modes except (\mathbf{k},s) and $(-\mathbf{k},s)$. We now use the symmetry relations

$$\omega(\mathbf{k},s) = \omega(-\mathbf{k},s); \quad \mathbf{v}(-\mathbf{k},s) = -\mathbf{v}(\mathbf{k},s),$$

and the fact that

$$\begin{aligned} \langle N(\mathbf{k},s) \rangle &= \langle N(-\mathbf{k},s) \rangle, \\ \langle N(\mathbf{k}',s') N(\mathbf{k},s) \rangle &= \langle N(\mathbf{k}',s') \rangle \langle N(\mathbf{k},s) \rangle; \quad (\mathbf{k}',s') \neq (\mathbf{k},s). \end{aligned}$$

Thus, the summation in Eq. (6) is identically zero, and the other terms combine to give

$$\langle s_i s_j(\mathbf{k},s) \rangle = \hbar^2 \omega^2(\mathbf{k},s) v_i(\mathbf{k},s) v_j(\mathbf{k},s) \times [\langle N^2(\mathbf{k},s) \rangle - \langle N(\mathbf{k},s) \rangle^2]. \quad (7)$$

Upon integration over the time in Eq. (5) the thermal conductivity becomes

$$\kappa_{ij} = \hbar^2 (VkT^2)^{-1} \sum_{\mathbf{k},s} \tau(\mathbf{k},s) \omega^2(\mathbf{k},s) v_i(\mathbf{k},s) v_j(\mathbf{k},s) \times [\langle N^2(\mathbf{k},s) \rangle - \langle N(\mathbf{k},s) \rangle^2]. \quad (8)$$

Equations (7) and (8) can be expressed in terms of a heat capacity per unit volume per mode via a formula from fluctuation theory⁹

$$c(\mathbf{k},s) = \hbar^2 (VkT^2)^{-1} \omega^2(\mathbf{k},s) [\langle N^2(\mathbf{k},s) \rangle - \langle N(\mathbf{k},s) \rangle^2].$$

The thermal conductivity tensor becomes

$$\kappa_{ij} = \sum_{\mathbf{k},s} \tau(\mathbf{k},s) v_i(\mathbf{k},s) v_j(\mathbf{k},s) c(\mathbf{k},s). \quad (9)$$

This is the usual expression for the thermal conductivity in an anisotropic crystal.^{7,8} Not only is the form of the expression the same, but the relaxation time is identical to that obtained from the Boltzmann equation. Thus, we have shown that the correlation function formulation of transport theory gives in the relaxation time approximation the same results as the Boltzmann equation for phonon transport in crystals. Discussions of this have been given previously^{10,11} for a classical gas. However, it is not clear that these hold for phonon transport in solids. Further, our demonstration is quite simple. We might note that the two methods are equivalent for a wider class of problems than considered here. Any one-body operator can be expressed in terms of number operators. The above proof, therefore, applies to all systems for which the flux operator can be written in the manner of Eq. (3).

We now consider the problem of the elastic scattering of phonons by point imperfections in a crystal. We have in mind here imperfections such as isotopic mass variation, impurities, vacancies, and interstitials. In these cases the terms in the Hamiltonian causing scattering are quadratic in the creation and annihilation operators. It can be shown, then, that Eq. (4) reduces to^{7,8}

$$\frac{dn(\mathbf{k},s;t)}{dt} = \pm \sum_{\mathbf{k}',s'} W(\mathbf{k},s; \mathbf{k}',s') \times [n(\mathbf{k}',s';t) - n(\mathbf{k},s;t)] \quad (10)$$

(minus sign for negative times), where

$$\langle n | N(\mathbf{k},s;t) | n \rangle \equiv n(\mathbf{k},s;t).$$

⁹ R. C. Tolman, *Principles of Statistical Mechanics* (Oxford University Press, New York, 1938), p. 632.

¹⁰ M. S. Green, *J. Chem. Phys.* **20**, 1281 (1952); **22**, 398 (1954).

¹¹ H. S. Green, *J. Math. Phys.* **2**, 344 (1961).

This master equation is conventionally obtained by standard lowest order time-dependent perturbation theory. As such it holds over time intervals shorter than the relaxation time implied by the equation itself. However, Van Hove¹² has shown that the master equation is in fact true under certain conditions to all orders of the perturbation. Therefore, long-time solutions to Eq. (10) are valid.

The transition probability per unit time, $W(\mathbf{k}, s; \mathbf{k}', s')$, is symmetric in its indices. In addition if the point imperfections are randomly arranged in the crystal the transition probability in certain important cases has the symmetry property

$$W(\mathbf{k}, s; \mathbf{k}', s') = W(-\mathbf{k}, s; \mathbf{k}', s'). \quad (11)$$

That is, the transition probability for elastic scattering of phonons in a given mode is the same into modes of equal energy and opposite wave vector. This is true for example for the scattering of phonons by atoms of a different mass (isotopic scattering) or with atoms having a different near neighbor binding force.¹³

Writing Eq. (10) for $dn(-\mathbf{k}, s; t)/dt$ and then subtracting this equation from that for $dn(\mathbf{k}, s; t)/dt$, making use of Eq. (11), we obtain

$$\frac{d}{dt}[n(\mathbf{k}, s; t) - n(-\mathbf{k}, s; t)] = [n(\mathbf{k}, s; t) - n(-\mathbf{k}, s; t)]\tau[-\mathbf{k}, \mathbf{k}s]^{-1},$$

where

$$\begin{aligned} \tau[-\mathbf{k}, \mathbf{k}s]^{-1} &= \sum_{\mathbf{k}', s'} W(\mathbf{k}, s; \mathbf{k}', s') \\ &= \sum_{\mathbf{k}', s'} W(-\mathbf{k}, s; \mathbf{k}', s'). \end{aligned} \quad (12)$$

This equation may be integrated immediately giving

$$n(\mathbf{k}, s; t) - n(-\mathbf{k}, s; t) = [n(\mathbf{k}, s) - n(-\mathbf{k}, s)] \exp(t/\tau[-\mathbf{k}, \mathbf{k}s]). \quad (13)$$

Thus, the excess of phonons of equal energy but opposite wave-vector decay exponentially with a characteristic time $\tau[-\mathbf{k}, \mathbf{k}s]$. This is not a relaxation per mode.

¹² L. Van Hove, *Physica* **23**, 441 (1957).

¹³ P. G. Klemens, *Proc. Phys. Soc. (London)* **A68**, 1113 (1955).

Of course, one would not expect to obtain a relaxation per mode since elastic scattering alone cannot lead to thermal equilibrium.

We now show that this exact relationship, which holds for anisotropic as well as isotropic crystals, is sufficient to characterize the thermal conductivity. The correlation function may be written as

$$\begin{aligned} \langle s_i(0)s_j(t) \rangle &= V^{-1} \sum_{\mathbf{k} > 0, s} \hbar \omega(\mathbf{k}, s) v_j(\mathbf{k}, s) \\ &\quad \times \langle s_i(0)[N(\mathbf{k}, s; t) - N(-\mathbf{k}, s; t)] \rangle. \end{aligned}$$

Using Eq. (12) and Eq. (13) this becomes

$$\begin{aligned} \langle s_i(0)s_j(t) \rangle &= V^{-1} \sum_{\mathbf{k} > 0, s} \hbar \omega(\mathbf{k}, s) v_j(\mathbf{k}, s) \exp(t/\tau[-\mathbf{k}, \mathbf{k}s]) \\ &\quad \times \langle s_i(0)[N(\mathbf{k}, s) - N(-\mathbf{k}, s)] \rangle \\ &= \sum_{\mathbf{k}, s} \langle s_i(0)s_j(\mathbf{k}, s) \rangle \exp(t/\tau[-\mathbf{k}, \mathbf{k}s]). \end{aligned}$$

This is identical to Eq. (5). Equation (9) is again obtained just as with the single mode relaxation discussed earlier. Consequently, the expression for the thermal conductivity tensor is the same but with the meaning of the relaxation time altered.

Equation (13) can also be used in the Boltzmann equation calculation again giving the same result as the correlation function calculation.

For spherical energy surfaces and isotropic scattering,

$$\tau[-\mathbf{k}, \mathbf{k}s] = \tau(|\mathbf{k}|s).$$

The thermal conductivity, Eq. (9), then becomes a scalar quantity which is formally equivalent to the results obtained by the familiar Boltzmann transport equation calculation of the thermal conductivity due to the isotropic elastic scattering of phonons by randomly arranged point imperfections.^{7,8} Furthermore, we have shown that the thermal conductivity due to mass-difference and binding force scattering of phonons in *anisotropic* crystals with randomly arranged point defects is also given by Eq. (9) with the new relaxation time, $\tau[-\mathbf{k}, \mathbf{k}s]$, defined by Eq. (12).