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Solution of the general phonon Boltzmann equation: boundary and mass defect scattering

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Abstract. The phonon Boltzmann equation is considered in its general form in the presence of mass defect interactions and boundary scattering. A variational method is applied to calculate the phonon thermal conductivity for a non-metallic slab of finite thickness and fixed temperatures at its two faces. In comparison with previous work the present study has the advantage that the different phonon polarizations are taken into account. Moreover, it has been shown that the operator involved in the study is positive definite which, in turn, implies that the variational method yields an upper bound on the phonon thermal conductivity.

1. Introduction

It is characteristic of most theoretical work on the phonon thermal conductivity that one considers only the initial deviation from a phonon equilibrium distribution which is assumed to exist. The phonon Boltzmann equation can consequently be linearized by retaining terms up to the first order in the initial deviation. However, at very low temperatures the effect of three-phonon normal and umklapp processes is very weak and can be completely ignored. The elastic character of the dominant mass defect and boundary scattering does not tend to set up an equilibrium distribution at these temperatures. Accordingly the Boltzmann equation cannot be linearized in the above sense and the general form has to be used instead. Parrott [1] and Williams [2] investigated this problem for a non-metallic slab of thickness L and temperatures T_0 and T_L at its faces. The phonon-scattering mechanism was taken to be due to mass defect interactions and boundary scattering alone. The general form of the collision operator of mass defect scattering as well as the exact boundary conditions were taken into consideration. Parrott [1] obtained the solution by using a series of integral operators while Williams [2] applied a variational principle. In both treatments, however, phonon polarization has been entirely neglected and the calculations were performed for one average branch.

The aim of the present work is to re-investigate the problem considered by Parrott [1] and Williams [2] by taking into account the different acoustic phonon polarizations and to deal with the resulting complexity. The complexity arises owing to the existence of two coupled integrodifferential equations instead of one equation of a much simpler structure in [1,2]. The variational principle of Williams [2] has then been modified to obtain the solution and to calculate the heat flux and thermal conductivity. Furthermore, in [2] the sign of the operator involved in the variational method was not explored. Here we have shown that the more general operator of the present study is positive definite which, in turn, shows that the procedure yields an upper bound on the thermal conductivity.

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The present work is arranged in the following way. In section 2 the two coupled integrodifferential Boltzmann equations which relate the distributions of transverse and longitudinal acoustic phonons are derived. The general form of the solution of these two equations is then given. The variational approach applied is consequently presented in section 3. The calculation of the heat flux and the thermal conductivity is considered in section 4. The two limiting cases in which mass defect scattering is much stronger or much weaker than boundary scattering are investigated in more detail.

2. Solution of the general Boltzmann equation

The general form of the phonon Boltzmann equation is given by

$$\boldsymbol{v}_\nu \cdot \nabla N_\nu = \left.\frac{\partial N_\nu}{\partial t}\right|_{\mathrm{c}} \qquad \nu \equiv (\sigma, \boldsymbol{k}) \tag{1}$$

where σ and $\boldsymbol{k}$ are the phonon polarization and wavevector, respectively. Also, N_ν and $\boldsymbol{v}_\nu$ are the number and group velocity of phonons in the mode ν. $(\partial N_\nu/\partial t)|_{\mathrm{c}}$ is the rate of change in N_ν due to collisions. For mass defects,

$$\left.\frac{\partial N_\nu}{\partial t}\right|_{\mathrm{c}} = \sum_{\nu'} (N_{\nu'} - N_\nu) W_\nu^{\nu'} \tag{2}$$

where the transition probability $W_\nu^{\nu'}$ is defined by

$$W_\nu^{\nu'} = \frac{\pi \Gamma}{2N_0} \omega_\nu \omega_{\nu'} (\boldsymbol{e}_\sigma \cdot \boldsymbol{e}_{\sigma'})^2 \delta(\omega_{\nu'} - \omega_\nu) \tag{3a}$$

$$\Gamma = \sum_i f_i \left(1 - \frac{M_i}{M}\right)^2 \qquad M = \sum_i f_i M_i \tag{3b}$$

ω_ν and $\boldsymbol{e}_\sigma$ are the angular frequency and polarization vector corresponding to the mode ν, N_0 is the number of unit cells and f_i is the fraction of atoms of mass M_i. If dispersion is neglected, the $\boldsymbol{k}$-space is assumed to be isotropic and acoustic phonons are only considered; then

$$\boldsymbol{v}_\nu = v_\sigma \hat{\boldsymbol{k}} \qquad \omega_\nu = v_\sigma k \qquad \sigma \equiv \mathrm{t}, \mathrm{l} \tag{4}$$

where $\hat{\boldsymbol{k}}$ is a unit vector in the direction of $\boldsymbol{k}$, and t and l refer to the transverse and longitudinal branches. Also, following Parrott [1] and Williams [2] it will be assumed that the dimensions of the two faces of the slab are much larger than its thickness. They can thus be regarded as infinite planes and the variation in N_ν along the normal direction z may only be considered. The two equations which result by taking $\sigma \equiv \mathrm{t}, \mathrm{l}$ in (1) and (2) can consequently be expressed in the form

$$v_{\mathrm{t}} \mu \frac{\mathrm{d}N_{\mathrm{t}k}}{\mathrm{d}z} + N_{\mathrm{t}k} \sum_{k'} (2W_{\mathrm{t}k}^{\mathrm{t}k'} + W_{\mathrm{t}k}^{\mathrm{l}k'}) = \sum_{k'} (2N_{\mathrm{t}k'} W_{\mathrm{t}k}^{\mathrm{t}k'} + N_{\mathrm{l}k'} W_{\mathrm{t}k}^{\mathrm{l}k'}) \tag{5a}$$

$$v_{\mathrm{l}} \mu \frac{\mathrm{d}N_{\mathrm{l}k}}{\mathrm{d}z} + N_{\mathrm{l}k} \sum_{k'} (2W_{\mathrm{l}k}^{\mathrm{t}k'} + W_{\mathrm{l}k}^{\mathrm{l}k'}) = \sum_{k'} (2N_{\mathrm{t}k'} W_{\mathrm{l}k}^{\mathrm{t}k'} + N_{\mathrm{l}k'} W_{\mathrm{l}k}^{\mathrm{l}k'}) \tag{5b}$$

where $\mu = \cos\theta$ and θ is the angle between k and the z axis which is chosen as the polar direction. The summation over k' on the left- and right-hand sides of the above two equations can be changed into integration over the Debye sphere in the usual manner. At low temperatures, the upper limit of the integration over k' can be taken to be equal to infinity and the resulting integral can be performed by using the delta function in (3*a*). It can further be shown that

$$\int_{-1}^{1}\int_{0}^{2\pi}(e_\sigma\cdot e_{\sigma'})^2\,\mathrm{d}\mu'\,\mathrm{d}\phi' = \tfrac{4}{3}\pi \tag{6a}$$

which gives

$$\mathrm{average}(e_\sigma\cdot e_{\sigma'})^2 = \tfrac{1}{3} \tag{6b}$$

Consequently on using (6*a*) and (6*b*) respectively for the integrations on the left- and right-hand sides of equations (5*a*) and (5*b*) it follows after some manipulation that

$$\mu\frac{\mathrm{d}N_\mathrm{t}(k,z,\mu)}{\mathrm{d}z} + \frac{N_\mathrm{t}(k,z,\mu)}{l_\mathrm{t}(k)} = \frac{1}{2l_\mathrm{t}(k)}\frac{v^3}{3v_\mathrm{t}^3}N^0(k,z) \tag{7a}$$

and

$$\mu\frac{\mathrm{d}N_\mathrm{l}(k,z,\mu)}{\mathrm{d}z} + \frac{N_\mathrm{l}(k,z,\mu)}{l_\mathrm{l}(k)} = \frac{1}{2l_\mathrm{l}(k)}\frac{v^3}{3v_\mathrm{t}^3}N^0\left(\frac{k}{c},z\right) \tag{7b}$$

where

$$c = \frac{v_\mathrm{t}}{v_\mathrm{l}} \qquad \frac{3}{v^3} = \frac{2}{v_\mathrm{t}^3} + \frac{1}{v_\mathrm{l}^3} \tag{8a}$$

$$N^0(k,z) = \int_{-1}^{1}[2N_\mathrm{t}(k,z,\mu') + c^3N_\mathrm{l}(ck,z,\mu')]\,\mathrm{d}\mu' = 2N_\mathrm{t}^0(k,z) + c^3N_\mathrm{l}^0(ck,z) \tag{8b}$$

$$N_\sigma^0(k,z) = \int_{-1}^{1}N_\sigma(k,z,\mu')\,\mathrm{d}\mu' \qquad \sigma \equiv \mathrm{t,l}. \tag{8c}$$

Also, l_t and l_l are the mass defect scattering transverse and longitudinal mean free paths which are given by

$$l_\mathrm{t}^{-1}(k) = Av_\mathrm{t}^3k^4 \qquad l_\mathrm{l}^{-1}(k) = Av_\mathrm{l}^3k^4 \qquad A = \frac{\Omega\Gamma}{4\pi v^3} \tag{9}$$

Ω is the volume of the unit cell. It can further be shown from equation (9) that

$$l_\mathrm{l}^{-1}(ck) = cl_\mathrm{t}^{-1}(k) \qquad l_\mathrm{t}^{-1}\left(\frac{k}{c}\right) = \frac{1}{c}l_\mathrm{l}^{-1}(k). \tag{10}$$

If we then integrate equations (7*a*) and (7*b*) with respect to μ, replace k by ck in the second and use the first relation in (10) we find that

$$\frac{\mathrm{d}}{\mathrm{d}z}\int_{-1}^{1}\mu[2N_\mathrm{t}(k,z,\mu) + c^2N_\mathrm{l}(ck,z,\mu)]\,\mathrm{d}\mu = 0 \tag{11}$$

which, in turn, implies that the quantity

$$J(k) = \int_{-1}^{1} \mu[2N_{\rm t}(k, z, \mu) + c^2 N_{\rm l}(ck, z, \mu)]\,\mathrm{d}\mu \tag{12}$$

is independent of z. The two quantities $N^0(k, z)$ and $J(k)$ resemble the two quantities $N_0(x)$ and J, respectively, introduced by Williams [2] (equations (15) and (11)). If a single average polarization branch is considered the present quantities will be equal to three times those of Williams. Also, it will be shown in section 4 that $J(k)$ is the only basic quantity needed for the calculation of the heat flux and thermal conductivity.

Now equations (7*a*) and (7*b*) are two coupled linear first-order differential equations in z which have to be solved subject to the boundary conditions

$$\begin{aligned} N_\sigma(k, 0, \mu) &= N_\sigma^{>}(k, 0) = 1\Big/\left[\exp\left(\frac{\hbar v_\sigma k}{k_{\rm B} T_0}\right) - 1\right] \qquad \mu > 0 \\ N_\sigma(k, L, \mu) &= N_\sigma^{<}(k, L) = 1\Big/\left[\exp\left(\frac{\hbar v_\sigma k}{k_{\rm B} T_L}\right) - 1\right] \qquad \mu < 0 \end{aligned} \tag{13}$$

for $\sigma \equiv$ t, l. A similar procedure to that used by Parrott [1] can then be employed to express the solution of these two equations in the form

$$\begin{aligned} N_{\rm t}(k, z, \mu) &= N_{\rm t}^{>}(k, 0) \exp\left(\frac{-z}{\mu l_{\rm t}(k)}\right) + \frac{1}{2\mu l_{\rm t}(k)} \frac{v^3}{3v_{\rm t}^3} \\ &\quad \times \int_0^z N^0(k, z') \exp\left(\frac{-(z - z')}{\mu l_{\rm t}(k)}\right) \mathrm{d}z' \qquad \mu > 0 \end{aligned} \tag{14a}$$

$$\begin{aligned} &= N_{\rm t}^{<}(k, L) \exp\left(\frac{L - z}{\mu l_{\rm t}(k)}\right) - \frac{1}{2\mu l_{\rm t}(k)} \frac{v^3}{3v_{\rm t}^3} \\ &\quad \times \int_z^L N^0(k, z') \exp\left(\frac{z' - z}{\mu l_{\rm t}(k)}\right) \mathrm{d}z' \qquad \mu < 0 \end{aligned} \tag{14b}$$

and

$$\begin{aligned} N_{\rm l}(k, z, \mu) &= N_{\rm l}^{>}(k, 0) \exp\left(\frac{-z}{\mu l_{\rm l}(k)}\right) + \frac{1}{2\mu l_{\rm l}(k)} \frac{v^3}{3v_{\rm t}^3} \\ &\quad \times \int_0^z N^0\left(\frac{k}{c}, z'\right) \exp\left(\frac{-(z - z')}{\mu l_{\rm l}(k)}\right) \mathrm{d}z' \qquad \mu > 0 \end{aligned} \tag{15a}$$

$$\begin{aligned} &= N_{\rm l}^{<}(k, L) \exp\left(\frac{L - z}{\mu l_{\rm l}(k)}\right) - \frac{1}{2\mu l_{\rm l}(k)} \frac{v^3}{3v_{\rm t}^3} \\ &\quad \times \int_z^L N^0\left(\frac{k}{c}, z'\right) \exp\left(\frac{z' - z}{\mu l_{\rm l}(k)}\right) \mathrm{d}z' \qquad \mu < 0 \end{aligned} \tag{15b}$$

In [1] the analogous distribution function of the single average branch was obtained by using a series of integral operators. For large thicknesses Parrott's [1] result for thermal conductivity was found to be about 70% of the result obtained by the standard procedure. Williams [2] argued that this may be because Parrott's series might not converge in this limit. Williams applied instead a variational method which has led to the conventional result. In the following section the modifications needed to apply Williams' variational approach to the present case will be considered. We start here by deriving suitable expressions for the two basic quantities $N^0(k, z)$ and $J(k)$. Substitution of (14) and (15) into (8*b*), (8*c*) and (12) yields

$$N^0(k,z) = X(k,z) + \frac{1}{2l_t(k)}\frac{v^3}{3v_t^3}\int_0^L N^0(k,z')\left[2E_1\left(\frac{|z-z'|}{l_t(k)}\right) + c^4E_1\left(\frac{c|z-z'|}{l_t(k)}\right)\right]\mathrm{d}z' \tag{16}$$

$$\begin{aligned} J(k)[N_t^<(k,L) - N_t^>(k,0)] &= -\tfrac{1}{2}(2+c^2)\{[N_t^>(k,0)]^2 + [N_t^<(k,L)]^2\} \\ &\quad + 2N_t^>(k,0)N_t^<(k,L)\left[2E_3\left(\frac{L}{l_t(k)}\right) + c^2E_3\left(\frac{cL}{l_t(k)}\right)\right] \\ &\quad + \frac{1}{2l_t(k)}\frac{v^3}{3v_t^3}\int_0^L N^0(k,z)X(k,z)\,\mathrm{d}z \end{aligned} \tag{17}$$

where

$$\begin{aligned} X(k,z) &= N_t^>(k,0)\left[2E_2\left(\frac{z}{l_t(k)}\right) + c^3E_2\left(\frac{cz}{l_t(k)}\right)\right] \\ &\quad + N_t^<(k,L)\left[2E_2\left(\frac{L-z}{l_t(k)}\right) + c^3E_2\left(\frac{c(L-z)}{l_t(k)}\right)\right] \end{aligned} \tag{18}$$

and $E_n(z)$ are the exponential integrals [3]. In the derivation of the above equations we have used the first relation in (10) in addition to the relations

$$N_l^>(ck,0) = N_t^>(k,0) \qquad N_l^<(ck,L) = N_t^<(k,L). \tag{19}$$

Also the fact that $J(k)$ is independent of z has been utilized.

Parrott [1] and Williams [2] considered the case in which $\Delta T = T_0 - T_L$ is small compared with T_0 and T_L. Also, Williams [2] defined

$$T = \tfrac{1}{2}(T_0 + T_L) \qquad \text{and hence} \qquad T_0 = T + \tfrac{1}{2}\Delta T \qquad T_L = T - \tfrac{1}{2}\Delta T. \tag{20}$$

It can thus be shown by using a Taylor expansion and retaining the first-order terms in ΔT that

$$\begin{aligned} N_\sigma^>(k,0) &= \bar{N}_\sigma(k) + \tfrac{1}{2}\Delta T\, g_\sigma(k) \\ N_\sigma^<(k,L) &= \bar{N}_\sigma(k) - \tfrac{1}{2}\Delta T\, g_\sigma(k) \end{aligned} \qquad \sigma \equiv \mathrm{t, l} \tag{21}$$

where

$$\begin{aligned} g_\sigma(k) &= \frac{\hbar v_\sigma k}{k_\mathrm{B}T^2}\bar{N}_\sigma(k)[\bar{N}_\sigma(k) + 1] \\ \bar{N}_\sigma(k) &= 1\left[\exp\left(\frac{\hbar v_\sigma k}{k_\mathrm{B}T}\right) - 1\right]. \end{aligned} \tag{22}$$

Following Williams [2], $N^0_\sigma(k, z)$ can further be replaced by $\phi_\sigma(k, z)$ where

$$N^0_\sigma(k, z) = 2\bar{N}_\sigma(k) + \tfrac{1}{2}\Delta T\, g_\sigma(k)\phi_\sigma(k, z). \tag{23}$$

This, however, does not imply that an equilibrium distribution for the phonon system exists. Substitution of (23) in (8*b*) gives

$$N^0(k, z) = 2(2 + c^3)\bar{N}_t(k) + \tfrac{1}{2}\Delta T\, g_t(k)\phi(k, z) \tag{24}$$

where

$$\phi(k, z) = 2\phi_t(k, z) + c^3\phi_l(ck, z). \tag{25}$$

The two relations $\bar{N}_l(ck) = \bar{N}_t(k)$ and $g_l(ck) = g_t(k)$ have been used to obtain (24). It can consequently be shown that the equations analogous to (16) and (17) take the form

$$\phi(k, z) = Y(k, z) + \frac{1}{2l_t(k)}\frac{v^3}{3v_t^3}\int_0^L \phi(k, z')\left[2E_1\left(\frac{|z - z'|}{l_t(k)}\right) + c^4E_1\left(\frac{c|z - z'|}{l_t(k)}\right)\right]\mathrm{d}z' \tag{26}$$

and

$$J(k) = \tfrac{1}{4}\Delta T\, g_t(k)\left[2 + c^2 + 4E_3\left(\frac{L}{l_t(k)}\right) + 2c^2E_3\left(\frac{cL}{l_t(k)}\right)\right.$$
$$\left. - \frac{1}{2l_t(k)}\frac{v^3}{3v_t^3}\int_0^L \phi(k, z)Y(k, z)\,\mathrm{d}z\right] \tag{27}$$

$$Y(k, z) = 2E_2\left(\frac{z}{l_t(k)}\right) + c^3E_2\left(\frac{cz}{l_t(k)}\right) - 2E_2\left(\frac{L - z}{l_t(k)}\right) - c^3E_2\left(\frac{c(L - z)}{l_t(k)}\right). \tag{28}$$

3. Variational approach

As has been previously pointed out, the evaluation of heat flux and thermal conductivity depends mainly on the basic quantity $J(k)$. In this section, $J(k)$ will be calculated by modifying the variational method used by Williams [2]. The method will be applied to the case presented in equations (26)–(28). The more general equations (16)–(18) can also be used for such purpose but the calculations will be much more complicated. We first express equations (26) and (27) in the form

$$\hat{L}_k\phi(k, z) = Y(k, z) \tag{29}$$

and

$$J(k) = \tfrac{1}{4}\Delta T\, g_t(k)\left[2 + c^2 + 4E_3\left(\frac{L}{l_t(k)}\right) + 2c^2E_3\left(\frac{cL}{l_t(k)}\right) - \frac{1}{2l_t(k)}\frac{v^3}{3v_t^3}\langle\phi(k, z), Y(k, z)\rangle\right]. \tag{30}$$

The inner product $\langle , \rangle$ is defined by

$$\langle\psi(z), \theta(z)\rangle = \int_0^L \psi(z)\theta(z)\,\mathrm{d}z \tag{31}$$

and the operator $\hat{L}_k$ by

$$\hat{L}_k\psi(z) = \psi(z) - \frac{1}{2l_t(k)}\frac{v^3}{3v_t^3}\int_0^L \left[2E_1\left(\frac{|z-z'|}{l_t(k)}\right) + c^4 E_1\left(\frac{c|z-z'|}{l_t(k)}\right)\right]\psi(z')\,dz'. \tag{32}$$

It is readily shown that the operator $\hat{L}_k$ is symmetric with respect to the inner product $\langle\,,\rangle$ and thus

$$F(\psi(z)) = 2\langle\psi(z), Y(k,z)\rangle - \langle\psi(z), \hat{L}_k\psi(z)\rangle \tag{33}$$

is stationary about the value $F(\phi(k,z)) = \langle\phi(k,z), Y(k,z)\rangle$, where $\phi(k,z)$ is the exact solution of (29) and $\psi(z)$ is a variational trial function. The k-dependence of $\psi(z)$ is dropped since the variation approach is concerned with studying the z-dependence. If we further assume that $\psi(z)$ depends on one variational parameter ($\psi(z) \equiv a\psi(z)$), then

$$F(\psi(z)) = \langle\psi(z), Y(k,z)\rangle^2/\langle\psi(z), \hat{L}_k\psi(z)\rangle. \tag{34}$$

The inner product in equation (30) can then be replaced by the stationary value of $F(\psi(z))$ evaluated with a suitable choice of $\psi(z)$. In this connection, one can easily show from (29) that $\phi(k,z)$ is odd in the sense that

$$\phi(k, L-z) = -\phi(k,z). \tag{35}$$

The trial function $\psi(z)$ should satisfy the same property in order to resemble the exact solution.

In the following we show that the operator $\hat{L}_k$ is positive definite with respect to the inner product $\langle,\rangle$ for odd functions $\psi(z)$ which satisfy (35). This point was not investigated by Williams [2]. We thus start by considering the simpler form of $\hat{L}_k$ used by Williams [2] which can be obtained from (32) by taking $v_l \equiv v_t \equiv v$, $l_l \equiv l_t \equiv l$ and $c = 1$. Hence

$$\hat{L}_k^{(W)}\psi(z) = \psi(z) - \frac{1}{2l(k)}\int_0^L E_1\left(\frac{|z-z'|}{l(k)}\right)\psi(z')\,dz' \tag{36}$$

and

$$\langle\psi(z), \hat{L}_k^{(W)}\psi(z)\rangle = \int_0^L \psi^2(z)\,dz - \frac{1}{2l(k)}\int_0^L\int_0^L E_1\left(\frac{|z-z'|}{l(k)}\right)\psi(z)\psi(z')\,dz\,dz' \tag{37a}$$

$$= \int_0^L \psi^2(z)\,dz - \frac{1}{l(k)}\int_0^{L/2}\int_0^{L/2}\psi(z)\psi(z')\left[E_1\left(\frac{|z-z'|}{l(k)}\right) - E_1\left(\frac{L-z-z'}{l(k)}\right)\right]dz\,dz'. \tag{37b}$$

The second term in (37b) is obtained by dividing the integrals in the second term of (37a) into four parts and then using the relevant transformations to change the integrals over the interval $[\frac{1}{2}L, L]$ to integrals over the interval $[0, \frac{1}{2}L]$. It is readily shown that the second term of (37b) is negative ($\psi(z)\psi(z')$ is positive for $z, z' \in [0, \frac{1}{2}L]$ owing to the argument used after equation (39)). One must, therefore, deal further with the negative part of this term in order to prove the positive definite property of $\hat{L}_k^{(W)}$. It can be shown after some manipulation and by using the relation $\psi(\frac{1}{2}L) = 0$ that

$$-\frac{1}{l(k)}\int_0^{L/2}\int_0^{L/2}\psi(z)\psi(z')E_1\left(\frac{|z-z'|}{l(k)}\right)\mathrm{d}z\,\mathrm{d}z' = -\int_0^L \psi^2(z)\,\mathrm{d}z - 2\int_0^{L/2}\mathrm{d}z\int_z^{L/2}\mathrm{d}z'\,\psi(z)\frac{\mathrm{d}\psi(z')}{\mathrm{d}z'}E_2\left(\frac{z'-z}{l(k)}\right). \tag{38}$$

Substitution of (38) in (37*b*) yields

$$\langle\psi(z), \hat{L}_k^{(W)}\psi(z)\rangle = -2\int_0^{L/2}\mathrm{d}z\int_z^{L/2}\mathrm{d}z'\psi(z)\frac{\mathrm{d}\psi(z')}{\mathrm{d}z'}E_2\left(\frac{z'-z}{l(k)}\right)\mathrm{d}z + \frac{1}{l(k)}\int_0^{L/2}\int_0^{L/2}\mathrm{d}z\,\mathrm{d}z'\psi(z)\psi(z')E_1\left(\frac{L-z-z'}{l(k)}\right). \tag{39}$$

Here $\psi(z)$ is taken to be a simple odd function which increases or decreases continuously as z increases in the interval $[0, L]$. It thus has one zero at $z = \frac{1}{2}L$. It follows consequently that the second part of (39) is positive since $\psi(z)$ and $\psi(z')$ have the same sign for $z, z' \in [0, \frac{1}{2}L]$. Furthermore $\mathrm{d}\psi(z')/\mathrm{d}z'$ is an even function which has a different sign from $\psi(z')$ for $z' \in [0, \frac{1}{2}L]$. Accordingly, the first part of (39) is also positive and therefore $\hat{L}_k^{(W)}$ is positive definite.

As regards the positive definite property of the present more complicated operator $\hat{L}_k$ (equation (32)), it can be proved in the same manner. It can be finally shown that

$$\langle\psi(z), \hat{L}_k\psi(z)\rangle = \frac{v^3}{3v_t^3}\int_0^{L/2}\mathrm{d}z\,\psi(z) \times\left\{-2\int_z^{L/2}\mathrm{d}z'\frac{\mathrm{d}\psi(z')}{\mathrm{d}z'}\left[2E_2\left(\frac{z'-z}{l_t(k)}\right)+c^3E_2\left(\frac{c(z'-z)}{l_t(k)}\right)\right] + \frac{1}{l_t(k)}\int_0^{L/2}\mathrm{d}z'\psi(z')\left[2E_1\left(\frac{L-z-z'}{l_t(k)}\right)+c^4E_1\left(\frac{c(L-z-z')}{l_t(k)}\right)\right]\right\}. \tag{40}$$

The right-hand side is positive, and accordingly $\hat{L}_k$ is positive definite. This, in turn, indicates that the exact solution of the Boltzmann equation maximizes $F(\psi(z))$ and accordingly minimizes $J(k)$ and the thermal conductivity. The procedure thus yields an upper bound on the thermal conductivity.

Williams [2] chose $\psi(z)$ in the form

$$\psi(z) = a(2z - L) \tag{41}$$

where the k-dependence of $\psi(z)$ may appear in the variational parameter a. This form possesses all the above-mentioned properties and will thus be used in the present work. It can consequently be shown after some lengthy calculations that

$$J(k) = \tfrac{1}{4}\Delta T\,g_t(k)\left(2 + c^2 + 4E_3(\bar{L}) + 2c^2E_3(c\bar{L}) + 2\frac{I_1^2}{I_2}\right) \tag{42}$$

where

$$I_1 = \tfrac{2}{3}(2+c) - \tfrac{1}{2}\bar{L}(2+c^2) - \bar{L}[2E_3(\bar{L}) + c^2E_3(c\bar{L})] - 2[2E_4(\bar{L}) + cE_4(c\bar{L})] \tag{43a}$$

$$I_2 = 3 - \tfrac{1}{2}\bar{L}^2(2+c^2) - \bar{L}^2[2E_3(\bar{L}) + c^2E_3(c\bar{L})] - 4\bar{L}[2E_4(\bar{L}) + cE_4(c\bar{L})] - 4[2E_5(\bar{L}) + E_5(c\bar{L})] \tag{43b}$$

and

$$\bar{L} = \bar{L}(k) = L/l_t(k). \tag{43c}$$

4. Calculation of the heat flux and the thermal conductivity

The phonon heat flux is given by [4]

$$Q = \frac{\hbar}{4\pi^2}\int_0^\infty k^3\,\mathrm{d}k\int_{-1}^{1}[2v_t^2N_t(k,z,\mu) + v_l^2N_l(k,z,\mu)]\mu\,\mathrm{d}\mu. \tag{44}$$

For the second part, we change the integration over k into integration over $k' = k/c$ and replace k' by k in the resulting form. It then follows by using (12) that

$$Q = \frac{\hbar v_t^2}{4\pi^2}\int_0^\infty J(k)k^3\,\mathrm{d}k. \tag{45}$$

Equation (45) gives the relation between the heat flux and the basic quantity $J(k)$. If we consequently substitute from (42) and (22) into (45) we obtain

$$Q = \frac{\hbar^2 v_t^3\Delta T}{16\pi^2 k_B T^2}\int_0^\infty k^4\frac{\exp(\hbar v_t k/k_B T)}{[\exp(\hbar v_t k/k_B T) - 1]^2}G(\bar{L})\,\mathrm{d}k \tag{46}$$

where

$$G(\bar{L}) = 2 + c^2 + 4E_3(\bar{L}) + 2c^2E_3(c\bar{L}) + \frac{2I_1^2}{I_2}. \tag{47}$$

In the above form, Q has been expressed in terms of v_t, $l_t(k)$ and the ratio $c = v_t/v_l$. An alternative form can also be obtained in a similar manner which gives Q in terms of v_l, $l_l(k)$ and c.

Williams [2] considered the two limiting cases in which the slab thickness is much larger or much smaller than the mean free path. The first case represents the situation in which the effect of mass defect interactions is much stronger than that of boundaries while the second stands for the situation in which the effect of the boundaries outweighs that of mass defect scattering. In the present work these two limits are represented by

$$\bar{L} \gg 1 \qquad \text{i.e. } L \gg l_t(k) > l_l(k) \tag{48a}$$

and

$$\bar{L}' \ll 1 \qquad \text{i.e. } L \ll l_l(k) < l_t(k) \qquad \text{then } \bar{L} \ll 1 \tag{48b}$$

where $\bar{L}' = L/l_l(k)$. In equations (48) we have utilized the fact that $v_t < v_l$ and hence $l_t(k) > l_l(k)$. Conditions (48) should, however, be satisfied for the whole effective range of integration over k. Since the integrand in equation (46) decays very rapidly at large values of k the integral can be cut at a certain maximum value k_{max} which is much less than the Debye radius at low temperatures. Condition (48*b*) can then be satisfied if $L \ll l_l(k_{max})$. On the other hand, condition (48*a*) cannot be satisfied for points in the neighbourhood of $k = 0$ for any large L, owing to the k^{-4}-dependence of $l_{t,l}(k)$. This point was not investigated by Williams [2] and was dealt with later by Simons [5] by applying a procedure analogous to that used by Mikhail and Simons [6, 7] for similar problems.

In the case in (48*a*) we first follow Williams and suppose that (48*a*) can be satisfied regardless of the k-dependence of $l_{t,l}(k)$. For the present calculations it can be shown after some algebra that

$$G(\bar{L}) = \frac{8}{3\bar{L}}(2 + c). \tag{49}$$

Substitution of (49) in (46) yields

$$Q = \frac{\hbar^2 v_t^3}{6\pi^2 k_B T^2}\frac{\Delta T}{L}\int_0^\infty \frac{k^4 \exp(\hbar v_t k/k_B T)}{[\exp(\hbar v_t k/k_B T) - 1]^2} l_t(k)(2 + c)\,dk. \tag{50}$$

The thermal conductivity is consequently given by

$$\kappa = \frac{Q}{\Delta T/L} = \frac{\hbar^2}{6\pi^2 k_B T^2}\sum_\sigma v_\sigma^4 \int_0^\infty \frac{k^4 \exp(\hbar v_\sigma k/k_B T)}{[\exp(\hbar v_\sigma k/k_B T) - 1]^2}\tau_\sigma(k)\,dk \tag{51}$$

where $\tau_\sigma(k) = l_\sigma(k)/v_\sigma$ and it stands for the relaxation time of mass defect scattering. Equation (51) is identical with the first term of the Callaway model [8, 9] which results owing to resistive processes. If we further substitute for $l_\sigma(k)$ from (9), then $\kappa \to \infty$ in agreement with the conventional result when the phonon-scattering mechanism is only due to mass defects.

In the more accurate treatment of Simons [5] the integral in equation (46) was divided into two parts. For the first part the following expansion has been used [10]:

$$\frac{y}{\exp y - 1} = \sum_{n=0}^\infty \frac{B_n y^n}{n!} \qquad |y| < 2\pi. \tag{52}$$

If the same approach is employed, it can be finally shown that

$$Q = \frac{k_B^4 T^3 \Delta T}{64\pi^2\hbar^3 v_t^2}\left(\frac{l_t(p_t)}{L}\right)^{3/4}\int_0^\infty \zeta^{-1/4}G(\zeta)\,d\zeta \tag{53a}$$

subject to the condition

$$L \gg l_t(p_t) \tag{53b}$$

where $p_t = k_B T/\hbar v_t$ and $G(\zeta)$ is defined by (47). Equation (53*a*) takes the same form as the result of Simons [5] but with a different definition for $G(\zeta)$. The integral involved in (53*a*) is finite since $\lim_{\zeta\to\infty}[G(\zeta)] = (8/3\zeta)(2+c)$ (equation (49)) while $G(0) = 2(2+c^2)$

(see equation (56) below). If we further suppose that the thermal conductivity κ can still be defined as $Q/(\Delta T/L)$, then

$$\kappa = \frac{k_B^4 T^3}{64\pi^2\hbar^3 v_t^2}[l_t(p_t)]^{3/4} L^{1/4} \int_0^\infty \zeta^{-1/4} G(\zeta)\,\mathrm{d}\zeta \tag{54}$$

which is finite for a slab of finite thickness. This gives a finite expression for the thermal conductivity when the phonon-scattering mechanism is dominated by mass defect scattering unlike the conventional result.

In the case in (48*b*) ($\bar{L} \ll 1$) we utilize the recurrence relation

$$zE_n(z) + nE_{n+1}(z) = \exp(-z) \qquad n = 1, 2, 3, \ldots \tag{55}$$

and expand the involved quantities in powers of $\bar{L}$. It can be finally shown that

$$G(\bar{L}) = 2(2 + c^2) \tag{56}$$

and

$$Q = \frac{\hbar^2 v_t^3 \Delta T}{8\pi^2 k_B T^2} \int_0^\infty \frac{k^4 \exp(\hbar v_t k/k_B T)}{[\exp(\hbar v_t k/k_B T) - 1]^2}(2 + c^2)\,\mathrm{d}k. \tag{57}$$

Moreover, by taking $\kappa = Q/(\Delta T/L)$, then

$$\kappa = \frac{\hbar^2}{6\pi^2 k_B T^2} \sum_\sigma v_\sigma^4 \tau_{\sigma b} \int_0^\infty \frac{k^4 \exp(\hbar v_\sigma k/k_B T)}{[\exp(\hbar v_\sigma k/k_B T) - 1]^2}\,\mathrm{d}k \tag{58}$$

where

$$\tau_{\sigma b} = \frac{3L}{4v_\sigma} \qquad \sigma \equiv \mathrm{t}, \mathrm{l}. \tag{59}$$

Again equation (58) is identical with the first term of the Callaway model when the different phonon polarizations are taken into account. Also, $\tau_{\sigma b}$ defines a relaxation time when phonon scattering is only due to the effect of boundaries. It takes the same form as the conventional relaxation time of boundary scattering [11] but with an effective specimen dimension $L_{\mathrm{eff}} = \frac{3}{4}L$, where L is the actual dimension. According to our knowledge this seems to be a new result which has not been noted by earlier workers.

5. Conclusions

The solution of the general Boltzmann equation obtained in the present work in the presence of mass defect and boundary scattering alone is a generalization for the results of earlier treatments by taking into consideration the different phonon polarizations. The variational approach applied has enabled us to deal with the resulting complexity. It further has the advantage that it confirms in a precise way that the calculated thermal conductivity is an upper bound on the exact value. The procedure yields a new form for the boundary scattering relaxation time when the phonon-scattering mechanism is dominated by boundary effects as well as a finite expression for the thermal conductivity when the effect of mass defect interactions is much stronger than that of boundary scattering.

References

[1] Parrott J E 1982 *J. Phys. C: Solid State Phys.* **15** 6919–24
[2] Williams M M R 1983 *J. Phys. C: Solid State Phys.* **16** 3707–12
[3] Morse P M and Feshbach H 1953 *Methods of Theoretical Physics* (New York: McGraw-Hill) p 1617
[4] Ziman J M 1960 *Electrons and Phonons* (Oxford: Clarendon)
[5] Simons S 1984 *Phys. Status Solidi* b **121** K109–12
[6] Mikhail I F I and Simons S 1975 *J. Phys. C: Solid State Phys.* **8** 3068–86
[7] Mikhail I F I and Simons S 1975 *J. Phys. C: Solid State Phys.* **8** 3087–107
[8] Callaway J 1959 *Phys. Rev.* **113** 1046–51
[9] Parrott J E 1971 *Phys. Status Solidi* b **48** K159–61
[10] Abramowitz M and Stegun I A 1972 *Handbook of Mathematical Functions* (New York: Dover)
[11] Casimir H B G 1938 *Physica* **5** 495