

## Anharmonic relaxation of phonons

G P SRIVASTAVA\*

Physics Department, Banaras Hindu University, Varanasi 221005

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**Abstract.** Using the Ziman scheme of considering a drifting Planck's distribution as the eigenvector of the linearized phonon collision operator, the anharmonic relaxation of phonons is discussed. The earlier arbitrariness in the phonon-phonon coupling parameters is removed by formulating explicit expressions for different allowed processes in terms of measurable quantities. Low and high temperature approximations of relaxation rates are also discussed; the results differ from earlier calculations. At low temperatures superthermal or high frequency phonons, which have temperature-independent and equal N- and U-relaxation rates, play important roles in thermal conduction in pure insulators.

**Keywords.** Anharmonicity; lattice thermal conductivity; phonon relaxation.

### 1. Introduction

Anharmonicity in lattice potential causes interaction among phonons. This many body interaction is highly complicated. Direct information regarding such interactions is meagre. Ultrasonic attenuation experiments do not deal with thermal phonons. Second-sound measurements may be useful to some extent, but are insufficient for the study. One can, of course, extract some information about relaxation rates of phonons by studying both thermal conductivity and second-sound results.

The general anharmonic inelastic interactions among the phonons cannot be treated by a relaxation time method. But assuming that the remaining phonons are in equilibrium, we can treat the interaction by a relaxation time approach. This has indeed been done by many workers dealing with the relaxation time approach. Frequency and temperature dependences of three-phonon relaxation rates have been discussed by many workers (for example, Herring 1954, Klemens 1958, Ziman 1960, Guthrie 1966). But unfortunately there has been no unanimous agreement in both low and high temperature regions. Almost every worker has taken the form of the relaxation rate as  $\tau_{\text{3ph}}^{-1} \propto g(\omega)f(T)$ . The form of  $g(\omega)$  is taken as some power of frequency;  $g(\omega) = \omega^n$ , and the exponent  $n$  for different polarization modes is adjusted to explain the experiments. Similarly  $f(T)$  is taken as  $AT^m$  and the exponent  $m$  is approximated at low and high temperatures and the parameter  $A$  assigned either temperature dependent or independent values in order to explain the results.

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\* Presently working as University of Wales Fellow in the Applied Physics Department, UWIST Cathays Park, Cardiff CF1 3NU, U.K.

The ad hoc forms of  $g(\omega)$  and  $f(T)$  should obviously be investigated further. Guthrie (1966) was the first to take into account the continuous function over the whole temperature region of thermal conductivity results. As a matter of fact, he suggested a form for  $\tau_{3\text{ph}}$  as

$$\tau_{3\text{ph}}^{-1} \propto g(\omega) T^{m(T)}$$

saying that  $f(T)$  should be expressed as a power of temperature, with the exponent  $m$  itself as a continuous function of temperature. He showed that  $m$  has both upper and lower bounds for both  $N$  and  $U$  processes—these bounds merging to unity at high temperatures. Sharma, Dubey and Verma (1971) (SDV model) used the approach of Guthrie by taking average values of  $m(T)$  for different polarization modes undergoing different types of attenuation mechanisms. Though the SDV model is recent and successful it is very hard to give a justification to various parameters which are empirically adjusted.

The present paper is an attempt to obtain explicit expressions for relaxation rates of phonons in different modes undergoing different kinds of three-phonon processes. The ambiguity in the choice of the adjustable parameters is solved by the recent development (Hamilton and Parrott 1969) in the knowledge of scattering strengths for different three-phonon processes. The frequency and temperature dependences of the relaxation rates are discussed under low and high temperature approximations. The results, apart from exact forms for the parameters, are in some contrast to the earlier works. In case of pure insulators the question of failure of Ziman limit of resistanceless  $N$ -processes is solved by supporting the view (Benin 1971) that high frequency phonons near Brillouin zone boundary have  $\tau_N \approx \tau_U$  and produce much heat even at an arbitrary low temperature.

## 2. Phonon collision aperture and relaxation rates

The rate of change of the distribution function  $N$  of phonons  $q$  ( $\equiv qs$ ), undergoing a three-phonon process, is given by (Srivastava 1973)

$$\begin{aligned} -\left. \frac{dN_q}{dt} \right|_{3\text{ph}} &= (P\vec{\Phi})_q \\ &= \sum_{q''q'''} [\frac{1}{2} \delta_{qq'} (\bar{P}_{qq''q'''} + \bar{P}_{q''q''',q} + \bar{P}_{q''',q''}) \\ &\quad + \delta_{q'q'''} (\bar{P}_{qq''q'''} + \bar{P}_{q''q''',q} + \bar{P}_{q''',q''})] \Phi_{q'} \\ &= T_{qa} \Phi_a + \sum_{q' \neq q} L_{aq'} \Phi_{q'} \end{aligned} \quad (1)$$

$-q \equiv (-qs)$ . The above picture for the rate of change of phonons uses Ziman's scheme (Ziman 1960) of defining

$$\begin{aligned} N_{\pm a} &= [\exp(A\omega_a - \Phi_{\pm a}) - 1]^{-1} \\ &\simeq \bar{N}_a + \Phi_{\pm a} \bar{N}_a (\bar{N}_a + 1) \end{aligned} \quad (2)$$

with  $\Phi_a = -q \cdot \nabla T/T$ , i.e., an odd function of the wave vector  $q$ . Also, by definition of a single mode relaxation rate, we have

$$\begin{aligned} -\left. \frac{dN_q}{dt} \right|_{\text{coll}} &= \frac{N_q - \bar{N}_q}{\tau_q} \\ &\simeq \frac{\bar{N}_q (\bar{N}_q + 1) \Phi_q}{\tau_q} \end{aligned} \quad (3)$$

Comparison of eqs (1) and (3) shows that a single mode anharmonic relaxation rate of phonons can be described in terms of the diagonal part of the (projection on the subspace of odd eigenvector  $\Phi_a$ ) collision operator  $P$ , provided that other phonons are supposed to be in equilibrium, *i.e.*, if one sets  $\Phi_{\mathbf{q}'\neq\mathbf{q}} = 0$ . One gets

$$\begin{aligned}\tau_a^{-1} &= \frac{1}{\bar{N}_a(\bar{N}_a + 1)} T_{aa} \\ &= \frac{1}{2} \sum_{a'a''} Q_{aa'a''} \left[ \frac{\bar{N}'\bar{N}''}{\bar{N}} \delta(\omega - \omega' - \omega'') \right. \\ &\quad \left. + 2 \frac{\bar{N}'(\bar{N}'' + 1)}{(\bar{N} + 1)} \delta(\omega + \omega' - \omega'') \right] \quad (4)\end{aligned}$$

where  $Q_{aa'a''}$  is related to the equilibrium transition rates given by (Srivastava 1973, Hamilton and Parrott 1969)

$$\bar{P}_{aa'a''} = \frac{\pi\hbar}{4\rho^3 N_0 \Omega} \frac{q^2 q'^2 q''^2}{\omega \omega' \omega''} |A_{aa'a''}|^2 \bar{N}' \bar{N}'' (\bar{N}'' + 1) \delta(\omega + \omega' - \omega'') \cdot \delta_{\mathbf{q}+\mathbf{q}'+\mathbf{q}'', \mathbf{G}}$$

Clearly  $Q_{aa'a''}$  involves the momentum conservation factor, *viz.*, the Kronecker delta  $\delta_{\mathbf{q}+\mathbf{q}'+\mathbf{q}'', \mathbf{G}}$ . Here  $\rho$  is the mass density,  $\Omega$  is the volume of a unit cell,  $N_0$  is number of unit cells present and  $\mathbf{G}$  is a reciprocal lattice vector.  $|A_{aa'a''}|^2$  are the three-phonon scattering strengths and depend on the directions of  $\mathbf{q}$ ,  $\mathbf{q}'$  and  $\mathbf{q}''$ , and on the second and third-order elastic constants of the crystal.

The three-phonon scattering strengths are, of course, very difficult to calculate. Hamilton and Parrott (1969) have calculated them for the first time in the isotropic case. Srivastava, Singh and Verma (1971, 1973) have extended their procedure to calculate  $|A_{aa'a''}|^2$  for different allowed processes in case of a simple cubic crystal. Once the three-phonon scattering strengths are calculated for the desired crystal class, and if the mass density  $\rho$  is known, one can obtain expressions for the relaxation rates for different three-phonon processes by evaluating the sums in eq. (4). It should be noted that evaluation of the sums for  $U$ -processes requires knowledge of a reciprocal lattice vector  $\mathbf{G}$ . Knowledge of a real reciprocal lattice vector for a three-dimensional crystal is meagre. The problem can be solved by adopting the grafting technique of Parrott (1963) who takes  $\mathbf{G}$  to be a pseudo-reciprocal vector of the magnitude of Debye diameter directed along  $(\mathbf{q} + \mathbf{q}')$ .

Both for  $N$ - and  $U$ -processes we see that  $\tau_a^{-1}$  can be broken up into two parts:— $\tau_{a, \text{class I}}^{-1}$  which is due to attenuation of phonons ( $qs$ ) by combination with phonons ( $q's'$ ) to give ( $q''s''$ ), and  $\tau_{a, \text{class II}}^{-1}$  which is due to anharmonic decay of phonons ( $qs$ ) into two others. In accordance with the energy selection rules  $\tau_{a, \text{class II}}^{-1}$  is contributed by  $s = L$  only. Summations over  $s'$  and  $s''$  allow us to write

$$\begin{aligned}\tau_{s, \text{class II}}^{-1} &= \tau_{qL, \text{class II}}^{-1} \\ &= \tau_{qL}^{-1}(L \rightarrow L + L) + 4\tau_{qL}^{-1}(L \rightarrow L + T) \\ &\quad + 4\tau_{qL}^{-1}(L \rightarrow T + T) \quad (5)\end{aligned}$$

$$\tau_{qs, \text{class I}}^{-1} = \tau_{qS}^{-1}(s + L \rightarrow L) + 2\tau_{qS}^{-1}(s + T \rightarrow L) \quad (6)$$

so that

$$\tau_{qT, \text{class I}}^{-1} = \tau_{qT}^{-1}(T + L \rightarrow L) + 2\tau_{qT}^{-1}(T + T \rightarrow L)$$

and

$$\tau^{-1}_{\mathbf{qL}, \text{class I}} = \tau_{\mathbf{qL}}^{-1}(L + L \rightarrow L) + 2 \tau_{\mathbf{qL}}^{-1}(L + T \rightarrow L)$$

In eqs (5) and (6) we use the following notations

$$\tau_{\mathbf{qS}}^{-1}(s + s' \rightarrow s'') = \sum_{\mathbf{q}'\mathbf{q}''} Q_{\mathbf{q}\mathbf{q}'\mathbf{q}''} \frac{\bar{N}'(\bar{N}'' + 1)}{(\bar{N} + 1)} \delta(\omega + \omega' - \omega'') \quad (7)$$

and

$$\tau_{\mathbf{qS}}^{-1}(s \rightarrow s' + s'') = \frac{1}{2} \sum_{\mathbf{q}'\mathbf{q}''} Q_{\mathbf{q}\mathbf{q}'\mathbf{q}''} \frac{\bar{N}'\bar{N}''}{\bar{N}} \delta(\omega - \omega' - \omega'') \quad (8)$$

From

$$\tau_{\mathbf{q}}^{-1} = \tau_{\mathbf{q}, \text{class I}}^{-1} + \tau_{\mathbf{q}, \text{class II}}^{-1}$$

we obtain

$$\begin{aligned} \tau_{\mathbf{qL}}^{-1} &= \tau_{\mathbf{qL}}^{-1}(L \rightarrow L + L) + \tau_{\mathbf{qL}}^{-1}(L + L \rightarrow L) + 4 \tau_{\mathbf{qL}}^{-1}(L \rightarrow L + T) \\ &\quad + 4 \tau_{\mathbf{qL}}^{-1}(L \rightarrow T + T) + 2 \tau_{\mathbf{qL}}^{-1}(L + T \rightarrow L) \end{aligned} \quad (9)$$

$$\tau_{\mathbf{qT}}^{-1} = \tau_{\mathbf{qT}}^{-1}(T + L \rightarrow L) + 2 \tau_{\mathbf{qT}}^{-1}(T + T \rightarrow L) \quad (10)$$

Let us evaluate the sums in eqs (7) and (8). The energy and momentum conservation relations can be represented by a single equation

$$a\mathbf{q} \pm a'\mathbf{q}' = q_D(1 - \epsilon) + \epsilon |\mathbf{q} + \mathbf{q}'| \quad (11)$$

where + and - signs represent Class I and Class II events respectively,  $\epsilon$  is for +1 for  $N$ -processes and -1 for  $U$ -processes. Here, as stated earlier, we have taken  $G = 2q_D(\mathbf{q} + \mathbf{q}')/|\mathbf{q} + \mathbf{q}'|$ ,  $q_D$  being Debye radius.  $a = c_s/c_{s''}$ ,  $a' = c_s/c_{s'}$ , where  $\omega_s(\mathbf{q}) = c_s(\mathbf{q}) \cdot \mathbf{q}$ , etc. If  $\theta'$  represents the angle between  $\mathbf{q}$  and  $\mathbf{q}'$ , the inequalities  $|\cos \theta'| \leq 1$  and  $q, q', q'' \leq q_D$ , yield, out of eq. (11), the following inequalities:

Class I events:

$$\left. \begin{aligned} 0, \frac{1-a}{1+a'} x \leq x' \leq \frac{1+a}{1-a'} x, \frac{1-ax}{a'} &, 1 \text{ for } N\text{-processes} \\ 0, \frac{2-(1+a)x}{1+a'} \leq x' \leq \frac{1-ax}{a'}, 1 & \quad \text{for } U\text{-processes} \end{aligned} \right\} \quad (12)$$

Class II events:

$$\left. \begin{aligned} 0, \frac{a-1}{a'+1} x, \frac{ax-1}{a'} \leq x' \leq \frac{a+1}{a'+1} x, \frac{a-1}{a'-1} x, 1 & \text{ for } N\text{-processes} \\ 0, \frac{(a+1)x-2}{a'+1} \leq x' \leq \frac{(a+1)x-2}{a'-1}, 1 & \quad \text{for } U\text{-processes} \end{aligned} \right\} \quad (13)$$

Here  $x = q/q_D$  and  $x' = q'/q_D$ . Removal of summation over  $\mathbf{q}''$  in the light of conservation relations, and change of summation over  $\mathbf{q}'$  into integrations over spherical co-ordinates  $(q', \theta', \phi')$  yield

$$\begin{aligned} \tau_{q_s}^{-1}(s + s' \rightarrow s'') &= \frac{\hbar q_D^5}{16\pi\rho a a'} \sum_{\epsilon} \int dx' x'^2 (ax + a'x') [1 - \epsilon \\ &+ \epsilon (ax + a'x')] \frac{\bar{N}'(\bar{N}'' + 1)}{(\bar{N} + 1)} \left| \frac{A_{qa'a''}}{\lambda + 2\mu} \right|^2 \end{aligned} \quad (14)$$

and

$$\begin{aligned} \tau_{q_s}^{-1}(s \rightarrow s' + s'') &= \frac{\hbar q_D^5 c_L^4}{32\pi\rho a a'} \sum_{\epsilon} \frac{1}{c_s'^4} \int dx' x'^2 (ax - a'x') [1 - \epsilon \\ &+ \epsilon (ax - a'x')] \frac{\bar{N}'\bar{N}''}{\bar{N}} \left| \frac{A_{qa'a''}}{\lambda + 2\mu} \right|^2 \end{aligned} \quad (15)$$

It should be noted here that the three phonon scattering strengths are assumed to be equal for both kinds of events and for allowed processes these are (Hamilton and Parrott 1969, Srivastava *et al.* 1971).

$$|A_{TTT}^{qq'q''}|^2 = 0 \quad (16 a)$$

$$\begin{aligned} |A_{TTL}^{qq'q''}|^2 &= \frac{1}{18} \{(\lambda + \mu + (\lambda + 3\mu + A + 2B) \cos 2\theta')^2 + \\ &+ \{2(\lambda + B) \cos \theta' + (4\mu + A) \cos \theta'' \cos(\theta'' - \theta')\}^2\} \end{aligned} \quad (16 b)$$

$$|A_{TLL}^{qq'q''}|^2 = \frac{1}{2} (\lambda + 3\mu + A + 2B)^2 \sin^2(\theta' + \theta'') \cos^2(\theta'' - \theta') \quad (16 c)$$

$$|A_{LLL}^{qq'q''}|^2 = [3\lambda + 6\mu + 2(A + 3B + C)]^2 \quad (16 d)$$

Here  $A$ ,  $B$  and  $C$  are related to third order elastic constants and  $\lambda$  and  $\mu$  are Lamé's constants.

### 3. Frequency and temperature dependence of $\tau_N$ and $\tau_v$

Frequency and temperature dependence of  $\tau_N$  and  $\tau_v$  for different polarization modes undergoing different kinds of processes can be discussed from eqs (14) and (15). One can always write

$$\tau_q^{-1} \propto G(\omega, T) \quad (17)$$

where  $G(\omega, T)$  is a non-simple continuous function over the entire frequency and temperature range. It would, therefore, be better to discuss low and high temperature approximations of  $G(\omega, T)$ .

At high temperatures  $\bar{N} \approx \frac{k_0 T}{\hbar \omega}$ , etc. Substitutions show that

$$\tau_s^{-1}(s + s' \rightarrow s'') \propto \omega T \left[ (1 - \epsilon) c_1 + \epsilon c_2 a \omega + \epsilon c_3 a' \right] \quad (18)$$

and

$$\tau_s^{-1}(s \rightarrow s' + s'') \propto \omega T \left[ (1 - \epsilon) c_1 + \epsilon c_2 a \omega - \epsilon c_3 a' \right]$$

which allow one to put down

$$\tau_{s, \text{high temp.}}^{-1} \propto g(\omega) f(T), \text{ with } f(T) = T \quad (19)$$

To discuss low temperature behaviour let us first consider  $N$ -processes. At low temperatures  $\bar{N} \approx e^{-A/\omega}$ ,  $A = \frac{\hbar}{k_0 T}$ , etc. For class II events we get

$$\tau_{s, N}^{-1}(s \rightarrow s' + s'') \propto \int dx' x'^2 (ax - a'x')^2 = [A - B\omega + C\omega^2] \quad (20)$$

For class I events

$$\tau_{s, N}^{-1}(s + s' \rightarrow s'') \propto \int dx' x'^2 (ax + a'x')^2 e^{-A\omega'}$$

which after using the integration result

$$\int_0^1 dx' x'^n e^{-A\omega'} \propto T^{n+1} \quad (21)$$

gives

$$\tau_{s, N}^{-1}(s + s' \rightarrow s'') = A\omega^2 T^3 + B\omega T^4 + cT^5 \quad (22)$$

Equations (20) and (22) allow us to write

$$\tau_{s, N, \text{low temp.}}^{-1} = Ag(\omega) + BG(\omega, T) \quad (23)$$

Now let us consider  $U$ -processes. In accordance with the energy and momentum selection rules there occurs a minimum value of  $\omega'$ , say  $\omega'_{\min}$ , below which  $U$ -processes do not occur: *i.e.*,  $\omega' \geq \omega'_{\min}$  for such processes to occur. Accordingly, we get, for class I events

$$\tau_{s, U}^{-1}(s + s' \rightarrow s'') \propto \int_{x_{\min}} dx' x'^2 (ax + a'x') (2 - ax - a'x') e^{-A\omega'}$$

There occur two cases. Let us consider the case when  $\omega' \geq \omega'_{\min} \neq 0$ . It is easy to show that

$$\tau_{s, U}^{-1}(s + s' \rightarrow s'') = e^{-A\omega'_{\min}} [A\omega^2 T^3 + B\omega T^4 + cT^5],$$

which can be put in the form

$$\tau_{s, U}^{-1}(s + s' \rightarrow s'') \propto e^{-A\omega'_{\min}} \cdot G(\omega, T) \quad (24)$$

More likely is the second case when  $\omega'_{\min} = 0$ . In this situation the integration result (21) yields

$$\tau_{s, U}^{-1}(s + s' \rightarrow s'') = T^3 [A\omega + B\omega^2] \quad (25)$$

which can be put in the form

$$\tau_{s, U}^{-1}(s + s' \rightarrow s'') \propto g(\omega) f(T), \quad f(T) = T^3 \quad (26)$$

Equations (24) and (25) tell that at low temperatures the relaxation rate of  $U$ -processes of class I kind varies at least as  $T^3$ , or exponentially.

For class II events we have

$$\begin{aligned} \tau_{s, U}^{-1}(s \rightarrow s' + s'') &\propto \int dx' x'^2 (ax - a'x') (2 - ax + a'x') \\ &\times \frac{\sinh(B\omega)}{\sinh(B\omega') \sinh(B\omega'')} \end{aligned}$$

where  $\omega_{s''}(q + q') = \omega_s(q) - \omega_{s'}(q')$ . For high frequency phonons ( $\hbar\omega \gg k_0 T$ ) we can approximate

$$\frac{\sinh(B\omega)}{\sinh(B\omega') \sinh(B\omega'')} \approx \text{const.} + \sum_{n=1}^{\infty} e^{-\beta n \omega'}$$

at low temperatures. This gives, with arguments as given above,

$$\begin{aligned} \tau_{s, U}^{-1}(s \rightarrow s' + s'') &= [Ag(\omega) + BT^3g(\omega)] \\ &\rightarrow \text{or may be } e^{-A\omega'_{\min}} \cdot G(\omega, T) \end{aligned} \quad (27)$$

Equations (24), (26) and (27) permit us to write

$$\tau_{s, v}^{-1} \text{ low temp.} = [Ag(\omega) + Bg(\omega)f(T)]$$

↓  
or may be  $e^{-A\omega'_{\min}} \cdot G(\omega, T)$

(28)

#### 4. Role of high-frequency phonons

Equations (20) and (27) show that at low temperatures there occurs a temperature independent term in the expression of  $\tau_s^{-1}$  ( $s \rightarrow s' + s''$ ). Of course  $\tau_N^{-1} \approx \tau_v^{-1}$  for such phonons, which decay spontaneously. This is the case of so-called superthermal or high frequency phonons ( $\hbar\omega \gg k_0T$ ). This means that even at very low temperatures  $U$ -processes always compete with  $N$ -process in case of high frequency phonons. Thus even for an infinite perfect crystal at arbitrary low temperature the belief that only the resistanceless  $N$ -processes exist (so-called the Ziman limit), is not correct. Benin (1971) also emphasises the role of such phonons, which under anharmonic interactions undergo the dominant attenuation mechanism, *viz.*, decay into two other phonons of equal energy. This decay is spontaneous for the processes  $L \rightarrow T + T$  and  $L \rightarrow L + T$ , for which if the longitudinal phonon has a large enough wave vector the contribution of  $U$ -processes is the same as that of  $N$ -processes.

The point of importance is that though high frequency phonons can have their life-times to be temperature independent and to be short as compared to that of thermal phonons ( $\hbar\omega \approx k_0T$ ), they are attenuated very rapidly and so develop much thermal resistance. Thus the contribution of  $U$ -processes should also be taken along with that of  $N$ -processes [which alone has been considered by Orbach and Vrederoe (1964)].

In eq. (22) the temperature independent term, *viz.*,  $g(\omega)$  may include the contribution  $\tau_{NL}^{-1} = B_L\omega^5$  as has been obtained by Slonimskii (1937). In eq (27) the term other than the constant one shows that decay of high frequency phonons is temperature dependent also—like  $T^3$  or  $e^{-A\omega'_{\min}}$ . This can be attributed to induced emission processes. Similarly, eq. (25) shows that absorption processes also bear a  $T^3$  or exponential temperature dependence, which can attenuate a thermal transverse mode more efficiently [see also Orbach and Vrederoe (1964)] and more or less at a rate at which a high frequency longitudinal mode is decayed by induced processes.

#### 5. Results and discussion

We have obtained explicit expressions for relaxation rates of phonons of different modes undergoing simplest type of anharmonic interactions, *viz.*, three-phonon processes in the Ziman limit. Contributions of high frequency phonons also has been discussed under the same limit (Ziman scheme of displaced Planck's distribution of phonon population above equilibrium). In contrast to earlier workers, we have been able to replace the arbitrary adjustable parameters describing coupling of phonons by scattering-strengths expressible in terms of known measurable quantities such as second and third-order elastic constants and mass density. With eqs (9) and (10) as the single-mode-relaxation rates one can calculate the thermal coefficient  $k$  by using a generalized form of Callaway (1959) as discussed by Parrott (1971):

$$\kappa = \frac{k_0}{6\pi^2} \left( \frac{k_0 T}{\hbar} \right)^3 \left\{ \sum_s \frac{1}{c_s} \int_0^{\Theta_s/T} \frac{\tau_N^s \tau_R^s}{\tau_N^s + \tau_R^s} \bar{N} (\bar{N} + 1) Z^4 dZ \right. \\ \left. + \frac{\left[ \sum_s \frac{1}{c_s^3} \int_0^{\Theta_s/T} \frac{\tau_R^s}{\tau_N^s + \tau_R^s} \bar{N} (\bar{N} + 1) Z^4 dZ \right]^2}{\sum_s \frac{1}{c_s^5} \int_0^{\Theta_s/T} \frac{\bar{N} (\bar{N} + 1)}{\tau_N^s + \tau_R^s} Z^4 dZ} \right\}$$

with  $Z = \hbar\omega/k_0T$  and  $\Theta_s = (\hbar q_v/k_0) c_s$ . Here  $\tau_R^s$  includes mass defect and boundary relaxation rates, which are easy to deal with. Here a non-dispersive isotropic model of crystal is considered, with Debye scheme of phonon specific heats.

It might be noted from eqs (19), (23) and (28) that the results obtained are of the form  $\tau_q^{-1} \alpha G(\omega, T)$ . Breaking up of the function  $G(\omega, T)$  into product of functions of frequency and temperature in the form  $G(\omega, T) = g(\omega) \cdot f(T)$  is not always possible, as has generally been done by almost all earlier workers in order to discuss frequency and temperature dependence of  $\tau_q^{-1}$ . We have ignored the frequency and temperature dependence of  $|A_{qq'q''}|^2$  in the discussion.

However, the difficult task of dealing with the anharmonic relaxation of phonons is not finished at this stage. The question arises: how true is it to consider the Planck displaced distribution of phonons as the eigenvector of the phonon collision operator? Certainly distribution of high frequency phonons, which play important role in thermal conduction of pure insulators at very low temperatures, is not a Ziman-like displaced Planck function; high frequency phonons drift at a slower rate than thermal phonons do. Benin (1971) considers the actual distribution to be made up of two displaced Planck functions:—one displaced distribution for thermal phonons and another for high frequency phonons which have a slower rate of deviation from equilibrium. But this is not the whole story. As a matter of fact the displaced distribution of the form  $\Phi_q = -\mathbf{q} \cdot \nabla T/T$  is relaxed only by  $U$ -processes, not by  $N$ -processes, and one should not deal with the whole matrix operator  $P$  simply with this eigenvector. The true relaxation times bear a complicated relationship with the phonon-collision operator  $P$ .

Hamilton (1973 *a*) has made an attempt to understand the nature of the eigenvectors of the matrix operator  $P$ . As a result he discovers that in the isotropic case one-third of the eigenvectors is associated with polarization directions which give local relaxation consisting of dissipation of entropy deficit. However, the eigenvectors he presents are not likely to be present in the application of thermal conductivity, and (only one-sixth) the eigenvectors containing non-zero crystal momentum only seriously affect the relationship.

The contribution of off-diagonal parts of the operator  $P$  has been neglected by earlier workers and in this work also (*viz.*, by setting  $\Phi_q = \Phi_{q''} = 0$ ). But contributions from off-diagonal part may not be too small to neglect—as a matter of fact, they may give contribution as high as equal to that given by diagonal part. Inclusion of such contributions is not easy. Hamilton (1973 *b*) has, however, considered this part, but has not been able to present any detailed result.

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