Theory of phonon-limited resistivity of metals including the effects of anharmonicity, Debye-Waller factor, and the multiphonon term

R. C. Shukla and E. R. Muller
Brock University, St. Catharines, Ontario L2S 3A1, Canada
(Received 5 September 1979)

The theory of phonon-limited resistivity ρ of metals is extended to include the effects of anharmonicity, Debye-Waller factor, and the first term of the multiphonon series. The double-time temperature-dependent Green's-function approach is used. All the relevant Green's functions involving two-, three-, and four-phonon operators are obtained exactly. The contribution to ρ from the third-order correlation functions are identified with the interference term. The contribution to ρ from the fourth-order correlation functions are identified with the Debye-Waller factor and the first term of the multiphonon series. The anharmonic contributions to ρ arise from the cubic and quartic shifts of the phonons and the phonon width, which are obtained from the full anharmonic one-phonon Green's function. The interference term represents the explicit cubic anharmonic contribution to ρ. Our expressions are valid for all temperatures. In the high-temperature limit all these contributions to ρ are found to vary as T^2. Thus the formula for ρ in the high-temperature limit is found to be $\rho = AT + BT^2$, where the linear term arises from the harmonic theory.

I. INTRODUCTION

The phonon-limited resistivity of metals (ρ) has been computed by many workers employing the following expression:

$$\rho(T) = C' \sum_j \int_{<2k_F} d\vec{q}\, q |W(q)|^2 \beta |\vec{q}\cdot\vec{\epsilon}_{\vec{q}j}|^2 f(\beta\omega_{\vec{q}j}) , \tag{1.1a}$$

where $q = |\vec{q}|$ and

$$f^{-1}(\beta\omega_{\vec{q}j}) = [\exp(\beta\hbar\omega_{\vec{q}j}) - 1][1 - \exp(-\beta\hbar\omega_{\vec{q}j})] . \tag{1.1b}$$

In these equations $W(q)$ represents the screened electron-ion pseudopotential form factor and $\omega_{\vec{q}j}, \vec{\epsilon}_{\vec{q}j}$ are the phonon frequencies and associate eigenvectors for the mode $\vec{q}, j$. The integration over $\vec{q}$ extends beyond the first Brillouin zone out to a sphere of radius $2k_F$. The other constants are given by $\beta = (k_B T)^{-1}$, where k_B is the Boltzmann constant, T is the absolute temperature, and

$$C' = \frac{3\hbar\Omega_0}{16 M e^2 v_F^2 k_F^4} ,$$

where M is the ion mass, v_F the Fermi velocity, e the charge of the electron, $\hbar$ Planck's constant divided by 2π, and Ω_0 the volume per ion. This formula for $\rho(T)$ is of course applicable only to those metals which have a spherical Fermi surface of radius k_F.

The above expression has been derived by Baym[1] and Greene and Kohn[2] from the following general expression of ρ:

$$\rho(T) = C \int_{<2k_F} d\vec{q}\, q |W(q)|^2 \int_{-\infty}^{\infty} d\omega\, S(\vec{q}, \omega) \times \frac{\beta\omega}{e^{\beta\hbar\omega} - 1} , \tag{1.2}$$

where

$$C = (M/\hbar) C' ,$$

$$S(\vec{q}, \omega) = \frac{1}{2\pi N} \int_{-\infty}^{\infty} dt\, e^{i\omega t} \left\langle \sum_{ll'} \exp[-i\vec{q}\cdot\vec{X}_l(t)] \times \exp[i\vec{q}\cdot\vec{X}_{l'}(0)] \right\rangle , \tag{1.3}$$

and the angular bracket denotes the thermal average. $\vec{X}_l(t)$ is the instantaneous position of the ion. Equation (1.1) can be derived from Eq. (1.2) if the following assumptions are made:

(a) Only harmonic averaging is carried over all states in Eq. (1.3).

(b) The effect of the Debye-Waller factor and the multiphonon series is ignored.

We note that under these approximations the resistivity as given by Eq. (1.1) is proportional to T in the high-temperature limit.

Recently, Grimvall[3] has analyzed the constant-volume resistivity data as obtained by various experimental workers for K, Na, Cu, Ag, and Au in the high-temperature limit. His conclusions are that formula (1.1) overestimates ρ approximately by 10% in the high-temperature limit.

More recently, Shukla and Taylor[4] performed a first-principles calculation of ρ for K and Na in the temperature range 20 °K to melting based on formula (1.1). No parameters were adjusted to fit the experimental data, yet the agreement for K was better than 3% for all $T \geq 40$ °K and for Na better than 4% for all $T \geq 60$ °K.

These conclusions are in contrast to the findings of Grimvall,[3] who included, in his semiempirical analysis of ρ, other terms such as a term proportional to T^2 in the high-temperature limit.

In a recent paper[5] we have enumerated and summarized the contributions to resistivity from anharmonicity, the Debye-Waller factor, and the first term of the multiphonon series. However, no detailed derivation of these terms was given. The purpose of this paper is to present a complete Green's-function theory of phonon-limited resistivity which yields all the contributions proportional to T^2 in the high-temperature limit. Detailed expressions for ρ are required in order to compute the proportionality constant.

The plan of this paper is as follows: The calculation of ρ requires a knowledge of $S(\vec{q}, \omega)$. In Sec. II we evaluate the contribution to $S(\vec{q}, \omega)$ from two-, three-, and four-phonon operator correlation functions using the respective Green's functions. The two-operator Green's function includes the effects of the cubic and quartic anharmonic terms. The two types of three-operator Green's functions are evaluated and shown in Sec. III to make equal contributions to ρ. They represent an explicit anharmonic contribution from the cubic term in the Hamiltonian. The four-operator Green's functions are evaluated exactly in the harmonic approximation as the anharmonic terms produce a temperature dependence of T^n with $n > 2$ for ρ in the high-temperature limit. Two of the three-operator Green's functions are identified with the Debye-Waller contribution and the other with the multiphonon term. Green's functions involving more than four operators are ignored, as their contribution to ρ in the high-temperature limit is $O(T^n)$, where $n > 2$.

Section III contains the corresponding contributions to ρ evaluated at any temperature. All the contributions to ρ proportional to T^2 in the high-temperature limit are discussed in Sec. IV. The discussion and conclusions are presented in Secs. V and VI, respectively.

II. DETERMINATION OF $S(\vec{q},\omega)$

In order to determine $S(\vec{q}, \omega)$, we first substitute

$$\vec{X}_l(t) = \vec{R}_l(0) + \vec{U}_l(t) \tag{2.1}$$

in Eq. (1.3). In Eq. (2.1), $\vec{U}_l(t)$ is the displacement of the lth ion from its equilibrium position $\vec{R}_l(0)$. Here we represent the operator $\vec{U}_l(t)$ in the Heisenberg representation. Since the c number $\vec{R}_l(0)$ commutes with $\vec{U}_l(t)$, $S(\vec{q}, \omega)$ can be expressed as

$$S(\vec{q}, \omega) = \frac{1}{2\pi N} \int_{-\infty}^{+\infty} e^{i\omega t} \sum_{ll'} \exp\{-i\vec{q} \cdot [\vec{R}_l(0) - \vec{R}_{l'}(0)]\} \langle \exp[-i\vec{q} \cdot \vec{U}_l(t)] \exp[i\vec{q} \cdot \vec{U}_{l'}(0)] \rangle dt \,. \tag{2.2}$$

The thermal average in Eq. (2.2) is now, with respect to the following Hamiltonian, expressed in the second quantized notation:

$$H = H_0 + H_A \,, \tag{2.3}$$

where

$$H_0 = \sum_{\vec{q}j} \hbar\omega_{\vec{q}j} (a^\dagger_{\vec{q}j} a_{\vec{q}j} + \tfrac{1}{2}) \,,$$

$$H_A = \lambda \sum_{\vec{q}_1 j_1 \vec{q}_2 j_2 \vec{q}_3 j_3} V^3(\vec{q}_1 j_1, \vec{q}_2 j_2, \vec{q}_3 j_3) A_{\vec{q}_1 j_1} A_{\vec{q}_2 j_2} A_{\vec{q}_3 j_3} + \lambda^2 \sum_{\vec{q}_1 j_1 \vec{q}_2 j_2 \vec{q}_3 j_3 \vec{q}_4 j_4} \times V^4(\vec{q}_1 j_1, \vec{q}_2 j_2, \vec{q}_3 j_3, \vec{q}_4 j_4) A_{\vec{q}_1 j_1} A_{\vec{q}_2 j_2} A_{\vec{q}_3 j_3} A_{\vec{q}_4 j_4} \,.$$

The various symbols appearing in Eq. (2.3) are defined as follows: λ is an order parameter to be set equal to 1 at the end of the calculations, $a^\dagger_{\vec{q}j}$ and $a_{\vec{q}j}$ are the phonon creation and annihilation operators,

$$A_{\vec{q}j} = a^\dagger_{-\vec{q}j} + a_{\vec{q}j} \,, \quad V^3(\vec{q}_1 j_1, \vec{q}_2 j_2, \vec{q}_3 j_3) \,,$$

and

$$V^4(\vec{q}_1 j_1, \vec{q}_2 j_2, \vec{q}_3 j_3, \vec{q}_4 j_4) \,,$$

are the Fourier transforms of the anharmonic force constants defined explicitly in Ref. 6 and Born and

Huang.[7]

Expanding the product of exponentials in Eq. (2.2) and recalling that the operators $\vec{U}_l(t)$ and $\vec{U}_{l'}(0)$ do not commute, we get

$$\begin{aligned}\exp[-i\vec{q}\cdot\vec{U}_l(t)]\exp[i\vec{q}\cdot\vec{U}_{l'}(0)] = 1 + [-i\vec{q}\cdot\vec{U}_l(t) + i\vec{q}\cdot\vec{U}_{l'}(0)] &+ \Big\{\frac{1}{2!}[-i\vec{q}\cdot\vec{U}_l(t)]^2 + \frac{1}{2!}[i\vec{q}\cdot\vec{U}_{l'}(0)]^2 \\ &\quad + [-i\vec{q}\cdot\vec{U}_l(t)][i\vec{q}\cdot\vec{U}_{l'}(0)]\Big\} \\ &+ \Big\{\frac{1}{3!}[-i\vec{q}\cdot\vec{U}_l(t)]^3 + \frac{1}{3!}[i\vec{q}\cdot\vec{U}_{l'}(0)]^3 + \frac{1}{2!}[-i\vec{q}\cdot\vec{U}_l(t)]^2[i\vec{q}\cdot\vec{U}_{l'}(0)] \\ &\quad + \frac{1}{2!}[-i\vec{q}\cdot\vec{U}_l(t)][i\vec{q}\cdot\vec{U}_{l'}(0)]^2\Big\} \\ &+ \Big\{\frac{1}{4!}[-i\vec{q}\cdot\vec{U}_l(t)]^4 + \frac{1}{4!}[i\vec{q}\cdot\vec{U}_{l'}(0)]^4 + \frac{1}{3!}[-i\vec{q}\cdot\vec{U}_l(t)]^3[i\vec{q}\cdot\vec{U}_{l'}(0)] \\ &\quad + \left(\frac{1}{2!}\right)^2[-i\vec{q}\cdot\vec{U}_l(t)]^2[i\vec{q}\cdot\vec{U}_{l'}(0)]^2 + \frac{1}{3!}[-i\vec{q}\cdot\vec{U}_l(t)][i\vec{q}\cdot\vec{U}_{l'}(0)]^3\Big\} + \cdots . \qquad (2.4)\end{aligned}$$

It is easily verified (for example, see Ref. 8) that the thermal averages, with respect to H [Eq. (2.3)], of all linear terms vanish. Following the same arguments one can show that the thermal averages, with respect to H, of all terms containing only odd powers of operators at equal time also vanish, and we obtain

$$\begin{aligned}&\langle\exp[-i\vec{q}\cdot\vec{U}_l(t)]\exp[i\vec{q}\cdot\vec{U}_{l'}(0)]\rangle \\ &\quad = 1 + \left\langle\Big\{\frac{1}{2!}[-i\vec{q}\cdot\vec{U}_l(t)]^2 + \frac{1}{2!}[i\vec{q}\cdot\vec{U}_{l'}(0)]^2 + \frac{1}{4!}[-i\vec{q}\cdot\vec{U}_l(t)]^4 + \frac{1}{4!}[i\vec{q}\cdot\vec{U}_{l'}(0)]^4 + \cdots\Big\}\right\rangle \\ &\quad + \left\langle[-i\vec{q}\cdot\vec{U}_l(t)][i\vec{q}\cdot\vec{U}_{l'}(0)]\right\rangle + \frac{1}{2!}\langle[-i\vec{q}\cdot\vec{U}_l(t)]^2[i\vec{q}\cdot\vec{U}_{l'}(0)]\rangle + \frac{1}{2!}\langle[-i\vec{q}\cdot\vec{U}_l(t)][i\vec{q}\cdot\vec{U}_{l'}(0)]^2\rangle \\ &\quad + \frac{1}{3!}\langle[-i\vec{q}\cdot\vec{U}_l(t)]^3[i\vec{q}\cdot\vec{U}_{l'}(0)]\rangle + \frac{1}{3!}\langle[-i\vec{q}\cdot\vec{U}_l(t)][i\vec{q}\cdot\vec{U}_{l'}(0)]^3\rangle + \left(\frac{1}{2!}\right)^2\langle\{[-i\vec{q}\cdot\vec{U}_l(t)][i\vec{q}\cdot\vec{U}_{l'}(0)]\}^2\rangle + \cdots . \qquad (2.5)\end{aligned}$$

Substituting (2.5) into (2.2), we get

$$S(\vec{q},\omega) = S_{el}(\vec{q},\omega) + S_2(\vec{q},\omega) + S_3(\vec{q},\omega) + S_4(\vec{q},\omega) + \cdots , \qquad (2.6)$$

where in Eq. (2.6) the subscript indicates the number of operators to be averaged, and $S_{el}(\vec{q},\omega)$ is the elastic part of $S(\vec{q},\omega)$ which arises from the equal-time operators in Eq. (2.5) and does not contribute to the resistivity. The other terms are

$$S_2(\vec{q},\omega) = \frac{1}{2\pi N}\int_{-\infty}^{\infty} e^{i\omega t}\sum_{ll'}\exp\{-i\vec{q}\cdot[\vec{R}_l(0)-\vec{R}_{l'}(0)]\}\langle[-i\vec{q}\cdot\vec{U}_l(t)][i\vec{q}\cdot\vec{U}_{l'}(0)]\rangle\, dt , \qquad (2.7)$$

$$\begin{aligned}S_3(\vec{q},\omega) = \frac{1}{2\pi N}\int_{-\infty}^{\infty} e^{i\omega t}\sum_{ll'}\exp\{-i\vec{q}\cdot[\vec{R}_l(0)-\vec{R}_{l'}(0)]\}&\Big\{\frac{1}{2!}\langle[-i\vec{q}\cdot\vec{U}_l(t)]^2[i\vec{q}\cdot\vec{U}_{l'}(0)]\rangle \\ &+ \frac{1}{2!}\langle[-i\vec{q}\cdot\vec{U}_l(t)][i\vec{q}\cdot\vec{U}_{l'}(0)]^2\rangle\Big\}dt , \qquad (2.8)\end{aligned}$$

$$\begin{aligned}S_4(\vec{q},\omega) = \frac{1}{2\pi N}\int_{-\infty}^{\infty} e^{i\omega t}\sum_{ll'}\exp\{-i\vec{q}\cdot[\vec{R}_l(0)-\vec{R}_{l'}(0)]\}&\Big\{\frac{1}{3!}\langle[-i\vec{q}\cdot\vec{U}_l(t)]^3[i\vec{q}\cdot\vec{U}_{l'}(0)]\rangle + \frac{1}{3!}\langle[-i\vec{q}\cdot\vec{U}_l(t)][i\vec{q}\cdot\vec{U}_{l'}(0)]^3\rangle \\ &+ \left(\frac{1}{2!}\right)^2\langle[-i\vec{q}\cdot\vec{U}_l(t)]^2[i\vec{q}\cdot\vec{U}_{l'}(0)]^2\rangle\Big\}dt . \qquad (2.9)\end{aligned}$$

To evaluate the expressions of S_2, S_3, and S_4 we need to express $\vec{U}_l(t)$ in terms of $A_{\vec{q}j}$, i.e.,

$$\vec{U}_l(t) = \left(\frac{\hbar}{2NM}\right)^{1/2}\sum_{\vec{q}j}\frac{\vec{\epsilon}_{\vec{q}j}}{(\omega_{\vec{q}j})^{1/2}}\exp[i\vec{q}\cdot\vec{R}_l(0)]A_{\vec{q}j}(t) . \qquad (2.10)$$

A. Calculation of $S_2(\vec{q},\omega)$

For the time being we concentrate on the simplification of $S_2(\vec{q}, \omega)$. Substituting $\vec{U}_l(t)$ into Eq. (2.7), we get

$$S_2(\vec{q}, \omega) = \frac{1}{2\pi N} \int_{-\infty}^{\infty} e^{i\omega t} \sum_{l l'} \exp\{-i\vec{q}\cdot[\vec{R}_l(0) - \vec{R}_{l'}(0)]\}\left(\frac{\hbar}{2NM}\right)$$
$$\times \sum_{\vec{q}_1 j_1 \vec{q}_2 j_2} \frac{(-i\vec{q}\cdot\vec{\epsilon}_{\vec{q}_1 j_1})(i\vec{q}\cdot\vec{\epsilon}_{\vec{q}_2 j_2})}{(\omega_{\vec{q}_1 j_1}\omega_{\vec{q}_2 j_2})^{1/2}} \exp[i\vec{q}_1\cdot\vec{R}_l(0)]\exp[i\vec{q}_2\cdot\vec{R}_{l'}(0)]\langle A_{\vec{q}_1 j_1}(t) A_{\vec{q}_2 j_2}(0)\rangle . \tag{2.11}$$

Interchanging the $\vec{q}$ sums with the l sums and using the property $\sum_l \exp[i\vec{Q}\cdot\vec{R}_l(0)] = N\delta_{\vec{Q},\vec{0}}$ and following the conventions $\vec{\epsilon}_{-\vec{q}j} = \vec{\epsilon}^{\,*}_{\vec{q}j}$, $\omega_{-\vec{q}j} = \omega_{\vec{q}j}$, and $A_{-\vec{q}j} = A^{\dagger}_{\vec{q}j}$, we obtain

$$S_2(\vec{q}, \omega) = \sum_{j_1 j_2} \left(\frac{N^2}{2\pi N}\right)\left(\frac{\hbar}{2NM}\right)\frac{(\vec{q}\cdot\vec{\epsilon}_{\vec{q}j_1})(\vec{q}\cdot\vec{\epsilon}^{\,*}_{\vec{q}j_2})}{(\omega_{\vec{q}j_1}\omega_{\vec{q}j_2})^{1/2}} \int_{-\infty}^{\infty} e^{i\omega t}\langle A_{\vec{q}j_1}(t) A^{\dagger}_{\vec{q}j_2}(0)\rangle dt . \tag{2.12}$$

The last integral is well known and can be evaluated employing the Green's-function method.[6,9] [Note in Ref. 6 Eq. (2.6) should read $J^{jj'}_{\vec{k}\vec{k}'}(t-t') = \langle A^{\dagger}_{\vec{k}'j'}(t') A_{\vec{k}j}(t)\rangle$.] For the Hamiltonian (2.3), we obtain[6]

$$J_{\vec{q}j_1 j_2}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{i\omega t}\langle A_{\vec{q}j_1}(t) A^{\dagger}_{\vec{q}j_2}(0)\rangle dt , \tag{2.13}$$

$$= -\lim_{\epsilon\to 0} \frac{2}{(1-e^{-\beta\hbar\omega})}\,\mathrm{Im}G_{\vec{q}j_1 j_2}(\omega + i\epsilon) , \tag{2.14}$$

$$= \frac{2\omega_{\vec{q}j_1}\delta_{j_1 j_2}}{\pi(1-e^{-\beta\hbar\omega})}\left(\frac{2\omega_{\vec{q}j_1}\Gamma_{\vec{q}j_1}(\omega)}{(\omega^2 - \Omega^2_{\vec{q}j_1})^2 + 4\omega^2_{\vec{q}j_1}\Gamma^2_{\vec{q}j_1}(\omega)}\right) , \tag{2.15}$$

where

$$\Omega^2_{\vec{q}j} = \omega^2_{\vec{q}j} + 2\omega_{\vec{q}j}\Delta_{\vec{q}j}(\omega) . \tag{2.16}$$

The symbols $\Delta_{\vec{q}j}(\omega)$ and $\Gamma_{\vec{q}j}(\omega)$ appearing in Eqs. (2.16) and (2.15), respectively, are the shift and width functions of a phonon of mode $\vec{q}j$ with the important property that they are even and odd functions of ω, respectively. They are defined as follows:

$$\Delta_{\vec{q}j}(\omega) = \Delta^{C}_{\vec{q}j}(\omega) + \Delta^{Q}_{\vec{q}j}(\omega) , \tag{2.17a}$$

where

$$\Delta^{C}_{\vec{q}j}(\omega) = 18\,\frac{\lambda^2}{\hbar^2}\sum_{\vec{q}_1 j_1 \vec{q}_2 j_2} |V^3(-\vec{q}j, \vec{q}_1 j_1, \vec{q}_2 j_2)|^2 \mathrm{P}[\tfrac{1}{2}F(\vec{q}_1 j_1, \vec{q}_2 j_2; \omega)] \tag{2.17b}$$

and

$$\Delta^{Q}_{\vec{q}j}(\omega) = 12\,\frac{\lambda^2}{\hbar}\sum_{\vec{q}_1 j_1} V^4(\vec{q}_1 j_1, -\vec{q}_1 j_1, \vec{q}j, -\vec{q}j) N_{\vec{q}_1 j_1} , \tag{2.17c}$$

with

$$F(\vec{q}_1 j_1, \vec{q}_2 j_2; \omega) = (N_{\vec{q}_1 j_1} + N_{\vec{q}_2 j_2})\left(\frac{1}{(\omega - \omega_{\vec{q}_1 j_1} - \omega_{\vec{q}_2 j_2})} - \frac{1}{(\omega + \omega_{\vec{q}_1 j_1} + \omega_{\vec{q}_2 j_2})}\right)$$
$$+ (N_{\vec{q}_2 j_2} - N_{\vec{q}_1 j_1})\left(\frac{1}{(\omega - \omega_{\vec{q}_1 j_1} + \omega_{\vec{q}_2 j_2})} - \frac{1}{(\omega + \omega_{\vec{q}_1 j_1} - \omega_{\vec{q}_2 j_2})}\right) \tag{2.17d}$$

and P stands for the principal part;

$$\Gamma_{\vec{q}j}(\omega) = \frac{18\pi\lambda^2}{\hbar^2}\sum_{\vec{q}_1 j_1 \vec{q}_2 j_2} |V^3(-\vec{q}j, \vec{q}_1 j_1, \vec{q}_2 j_2)|^2 G(\vec{q}_1 j_1, \vec{q}_2 j_2; \omega) , \tag{2.18a}$$

where

$$G(\vec{q}_1 j_1, \vec{q}_2 j_2; \omega) = \tfrac{1}{2}\{(N_{\vec{q}_1 j_1} + N_{\vec{q}_2 j_2})[\delta(\omega - \omega_{\vec{q}_1 j_1} - \omega_{\vec{q}_2 j_2}) - \delta(\omega + \omega_{\vec{q}_1 j_1} + \omega_{\vec{q}_2 j_2})]$$
$$+ (N_{\vec{q}_2 j_2} - N_{\vec{q}_1 j_1})[\delta(\omega - \omega_{\vec{q}_1 j_1} + \omega_{\vec{q}_2 j_2}) - \delta(\omega + \omega_{\vec{q}_1 j_1} - \omega_{\vec{q}_2 j_2})]\} , \tag{2.18b}$$

with

$N_{\vec{q}j} = \coth(\beta\hbar\omega_{\vec{q}j}/2)$.

Substituting Eq. (2.15) into Eq. (2.12), we obtain $S_2(\vec{q},\omega)$. We note that in the harmonic approximation $S_2(\vec{q},\omega)$ reduces to

$$S_2(\vec{q},\omega) = \sum_{j_1} \frac{\hbar}{2M} \frac{|\vec{q}\cdot\vec{\epsilon}_{\vec{q}j_1}|^2}{\omega_{\vec{q}j_1}} \frac{[\delta(\omega-\omega_{\vec{q}j_1}) - \delta(\omega+\omega_{\vec{q}j_1})]}{(1-e^{\beta\hbar\omega})},$$

which at first glance appears different from that quoted by other authors.[10,11] However, the expression given by the above equation and those obtained in Refs. 10 and 11 have the same value at $\omega = \omega_{\vec{q}j_1}$ and $-\omega_{\vec{q}j_1}$.

B. Calculation of $S_3(\vec{q},\omega)$

Using the same procedures as outlined in the calculation of $S_2(\vec{q},\omega)$, we find

$$S_3(\vec{q},\omega) = -S_3^A(\vec{q},\omega) + S_3^B(\vec{q},\omega)\,, \tag{2.19}$$

where

$$S_3^A(\vec{q},\omega) = \left(\frac{\hbar}{2NM}\right)^{3/2} \frac{iN}{2!} \sum_{\vec{q}_1\vec{q}_2 j_1 j_2 j} \frac{\Delta(\vec{q}-\vec{q}_1-\vec{q}_2)}{(\omega_{\vec{q}_1j_1}\omega_{\vec{q}_2j_2}\omega_{\vec{q}j})^{1/2}} (\vec{q}\cdot\vec{\epsilon}_{\vec{q}_1j_1})(\vec{q}\cdot\vec{\epsilon}_{\vec{q}_2j_2})(\vec{q}\cdot\vec{\epsilon}^{\,*}_{\vec{q}j}) \times \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}\langle A_{\vec{q}_1j_1}(t)A_{\vec{q}_2j_2}(t)A^{\dagger}_{\vec{q}j}(0)\rangle dt \tag{2.20}$$

and

$$S_3^B(\vec{q},\omega) = \left(\frac{\hbar}{2NM}\right)^{3/2} \frac{iN}{2!} \sum_{\vec{q}_1\vec{q}_2 j_1 j_2 j} \frac{\Delta(\vec{q}-\vec{q}_1-\vec{q}_2)}{(\omega_{\vec{q}_1j_1}\omega_{\vec{q}_2j_2}\omega_{\vec{q}j})^{1/2}} (\vec{q}\cdot\vec{\epsilon}_{\vec{q}j})(\vec{q}\cdot\vec{\epsilon}^{\,*}_{\vec{q}_1j_1})(\vec{q}\cdot\vec{\epsilon}^{\,*}_{\vec{q}_2j_2}) \times \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}\langle A_{\vec{q}j}(t)A^{\dagger}_{\vec{q}_1j_1}(0)A^{\dagger}_{\vec{q}_2j_2}(0)\rangle dt\,. \tag{2.21}$$

Shukla and Muller[6] have evaluated a similar integral to the one appearing in expression (2.20) for $S_3^A(\vec{q},\omega)$. Following their procedures we find

$$J_3^A(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}\langle A_{\vec{q}_1j_1}(t)A_{\vec{q}_2j_2}(t)A^{\dagger}_{\vec{q}j}(0)\rangle dt\,, \tag{2.22}$$

$$= -\lim_{\epsilon\to 0} \frac{2}{(1-e^{-\beta\hbar\omega})} \,\mathrm{Im} D_1^A(\omega+i\epsilon)\,, \tag{2.23}$$

where the Green's $D_1^A(\omega)$ is given by

$$D_1^A(\omega) = \frac{6\lambda}{4\pi\hbar} V^3(-\vec{q}_1j_1, -\vec{q}_2j_2, \vec{q}j) F(\vec{q}_1j_1, \vec{q}_2j_2;\omega)\left(\frac{1}{(\omega-\omega_{\vec{q}j})} - \frac{1}{(\omega+\omega_{\vec{q}j})}\right), \tag{2.24}$$

and $F(\vec{q}_1j_1, \vec{q}_2j_2;\omega)$ has been defined in Eq. (2.17c). We note here that to $O(\lambda)$ the extra terms arising in expression (2.24) of Ref. 6 cancel out exactly in the harmonic approximation.

Substituting for $D_1^A(\omega)$ in Eq. (2.23) and the resulting expression into Eq. (2.20), a typical term arising from the product

$$\left(\frac{1}{(\omega+\omega_{\vec{q}j})} \frac{1}{\omega-\omega_{\vec{q}_1j_1}-\omega_{\vec{q}_2j_2}}\right)$$

in the expression of $S_3^A(\vec{q},\omega)$ is

$$\left(\frac{\hbar}{2NM}\right)^{3/2}\left(\frac{iN}{2!}\right)\left(\frac{3\lambda}{\hbar}\right) \sum_{\vec{q}_1\vec{q}_2 j_1 j_2 j} \frac{\Delta(\vec{q}-\vec{q}_1-\vec{q}_2)}{(\omega_{\vec{q}_1j_1}\omega_{\vec{q}_2j_2}\omega_{\vec{q}j})^{1/2}} V^3(-\vec{q}_1j_1, -\vec{q}_2j_2, \vec{q}j)(\vec{q}\cdot\vec{\epsilon}_{\vec{q}_1j_1})(\vec{q}\cdot\vec{\epsilon}_{\vec{q}_2j_2})(\vec{q}\cdot\vec{\epsilon}^{\,*}_{\vec{q}j}) \times \frac{(N_{\vec{q}_1j_1}+N_{\vec{q}_2j_2})}{(1-e^{-\beta\hbar\omega})} \frac{\delta(\omega+\omega_{\vec{q}j}) - \delta(\omega-\omega_{\vec{q}_1j_1}-\omega_{\vec{q}_2j_2})}{(\omega_{\vec{q}j}+\omega_{\vec{q}_1j_1}+\omega_{\vec{q}_2j_2})}\,. \tag{2.25}$$

The other seven terms arising in $S_3^A(\vec{q},\omega)$ can be written in a similar fashion.

The contribution from the second term $S_3^B(\vec{q},\omega)$ in Eq. (2.19) can be found provided the Green's function

$$D_1^B(t) \equiv \langle\langle A_{\vec{q}j}(t); A^\dagger_{\vec{q}_1 j_1}(0)A^\dagger_{\vec{q}_2 j_2}(0)\rangle\rangle$$
$$= -i\Theta(t)\langle[A_{\vec{q}j}(t), A^\dagger_{\vec{q}_1 j_1}(0)A^\dagger_{\vec{q}_2 j_2}(0)]\rangle$$

is known, where $\Theta(t)$ is the Heaviside unit step function, the square bracket is the commutator, and the angular bracket denotes the thermal average. We have obtained this Green's function using the equation-of-motion method. Defining another Green's function,

$$D_2^B(t) \equiv \langle\langle B_{\vec{q}j}(t); A^\dagger_{\vec{q}_1 j_1}(0)A^\dagger_{\vec{q}_2 j_2}(0)\rangle\rangle ,$$

where $B_{\vec{q}j} = a_{\vec{q}j} - a^\dagger_{-\vec{q}j}$, and using the equations of motion of the operators $A_{\vec{q}j}$ and $B_{\vec{q}j}$ obtained from the Hamiltonian (2.3), we find

$$i\frac{d}{dt} D_1^B = \omega_{\vec{q}j} D_2^B \tag{2.26}$$

and

$$i\frac{d}{dt} D_2^B = \omega_{\vec{q}j} D_1^B + \frac{6\lambda}{\hbar}\sum_{\vec{q}_4\vec{q}_5 j_4 j_5} V^3(\vec{q}_4 j_4, \vec{q}_5 j_5, -\vec{q}j)E_1^B , \tag{2.27}$$

where E_1^B is the two-phonon Green's function

$$\langle\langle A_{\vec{q}_4 j_4}(t)A_{\vec{q}_5 j_5}(t); A^\dagger_{\vec{q}_1 j_1}(0)A^\dagger_{\vec{q}_2 j_2}(0)\rangle\rangle .$$

Since E_1^B arising in Eq. (2.27) multiplies a term of $O(\lambda)$, we evaluate it in the harmonic approximation and obtain

$$E_1^B = \frac{1}{2\pi} F(\vec{q}_4 j_4, \vec{q}_5 j_5; \omega)(\delta_{\vec{q}_4\vec{q}_1}\delta_{j_4 j_1}\delta_{\vec{q}_5\vec{q}_2}\delta_{j_5 j_2} + \delta_{\vec{q}_4\vec{q}_2}\delta_{j_4 j_2}\delta_{\vec{q}_5\vec{q}_1}\delta_{j_5 j_1}) , \tag{2.28}$$

where $F(\vec{q}_4 j_4, \vec{q}_5 j_5; \omega)$ is defined in Eq. (2.17d). Fourier transforming Eqs. (2.26) and (2.27) and making use of expression (2.28) for E_1^B, we obtain the following expression for $D_1^B(\omega)$:

$$D_1^B(\omega) = \frac{6\lambda}{4\pi\hbar} V^3(\vec{q}_1 j_1, \vec{q}_2 j_2, -\vec{q}j)F(\vec{q}_1 j_1, \vec{q}_2 j_2; \omega) \times\left(\frac{1}{\omega - \omega_{\vec{q}j}} - \frac{1}{\omega + \omega_{\vec{q}j}}\right) . \tag{2.29}$$

We use the definition

$$J_3^B(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}\langle A_{\vec{q}j}(t)A^\dagger_{\vec{q}_1 j_1}(0)A^\dagger_{\vec{q}_2 j_2}(0)\rangle dt$$
$$= -\lim_{\epsilon\to 0}\frac{2}{(1-e^{-\beta\hbar\omega})}\,\mathrm{Im}\, D_1^B(\omega + i\epsilon) , \tag{2.30}$$

substitute for $D_1^B(\omega)$, and extract the term similar to that given in expression (2.25). This corresponding term is

$$\left(\frac{\hbar}{2NM}\right)^{3/2}\left(\frac{iN}{2!}\right)\left(\frac{3\lambda}{\hbar}\right)\sum_{\vec{q}_1\vec{q}_2 j_1 j_2 j}\frac{\Delta(\vec{q}-\vec{q}_1-\vec{q}_2)}{(\omega_{\vec{q}_1 j_1}\omega_{\vec{q}_2 j_2}\omega_{\vec{q}j})^{1/2}} V^3(\vec{q}_1 j_1, \vec{q}_2 j_2, -\vec{q}j)(\vec{q}\cdot\epsilon^*_{\vec{q}_1 j_1})(\vec{q}\cdot\epsilon^*_{\vec{q}_2 j_2})(\vec{q}\cdot\epsilon_{\vec{q}j})$$
$$\times\frac{(N_{\vec{q}_1 j_1} + N_{\vec{q}_2 j_2})}{(1-e^{-\beta\hbar\omega})}\,\frac{\delta(\omega+\omega_{\vec{q}j}) - \delta(\omega - \omega_{\vec{q}_1 j_1} - \omega_{\vec{q}_2 j_2})}{(\omega_{\vec{q}j} + \omega_{\vec{q}_1 j_1} + \omega_{\vec{q}_2 j_2})} . \tag{2.31}$$

Careful comparison of the expressions (2.25) and (2.31) show that (a) owing to the summations over $\vec{q}_1$ and $\vec{q}_2$, these vectors can be changed to $-\vec{q}_1$ and $-\vec{q}_2$, respectively, without affecting the resulting sum, and (b) if in expression (2.25) $\vec{q}$ is changed to $-\vec{q}$, the resulting expression is identical to minus expression (2.31).

Careful pairwise comparison of the eight terms arising in $S_3^A(\vec{q},\omega)$ and $S_3^B(\vec{q},\omega)$ show that the properties (a) and (b) hold true for all corresponding pairs. We therefore conclude that

$$S_3^B(\vec{q},\omega) = -S_3^A(-\vec{q},\omega) . \tag{2.32}$$

Hence we can rewrite Eq. (2.19) as

$$S_3(\vec{q},\omega) = -[S_3^A(\vec{q},\omega) + S_3^A(-\vec{q},\omega)] . \tag{2.33}$$

Looking ahead to the contribution of $S_3(\vec{q},\omega)$ to the resistivity, we note that the q-dependent factors multiplying $S_3(\vec{q},\omega)$ in expression (1.2) are symmetric in q whence $S_3^A(\vec{q},\omega)$ and $S_3^A(-\vec{q},\omega)$ will yield equal contributions to ρ.

C. Calculation of $S_4(\vec{q},\omega)$

Following the procedures outlined in the calculations of $S_2(\vec{q},\omega)$ and $S_3(\vec{q},\omega)$, we find

$$S_4(\vec{q},\omega) = S_4^A(\vec{q},\omega) + S_4^B(\vec{q},\omega) + S_4^C(\vec{q},\omega) ,$$

where

$$S_4^A(\vec{q},\omega) = -\left(\frac{\hbar}{2NM}\right)^2 \frac{N}{3!} \sum_{\vec{q}_1\vec{q}_2\vec{q}_3 j_1 j_2 j_3 j} \frac{\Delta(-\vec{q}+\vec{q}_1+\vec{q}_2+\vec{q}_3)}{(\omega_{\vec{q}_1 j_1}\omega_{\vec{q}_2 j_2}\omega_{\vec{q}_3 j_3}\omega_{\vec{q}j})^{1/2}} (\vec{q}\cdot\vec{\epsilon}_{\vec{q}_1 j_1})(\vec{q}\cdot\vec{\epsilon}_{\vec{q}_2 j_2})(\vec{q}\cdot\vec{\epsilon}_{\vec{q}_3 j_3})(\vec{q}\cdot\vec{\epsilon}^{\,*}_{\vec{q}j})$$

$$\times \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}\langle A_{\vec{q}_1 j_1}(t) A_{\vec{q}_2 j_2}(t) A_{\vec{q}_3 j_3}(t) A^\dagger_{\vec{q}j}(0)\rangle\, dt , \tag{2.34}$$

$$S_4^B(\vec{q},\omega) = \left(\frac{\hbar}{2NM}\right)^2 \frac{N}{(2!)^2} \sum_{\vec{q}_1\vec{q}_2\vec{q}_3\vec{q}_4 j_1 j_2 j_3 j_4} \frac{\Delta(-q+q_1+q_2)\Delta(q-q_3-q_4)}{(\omega_{\vec{q}_1 j_1}\omega_{\vec{q}_2 j_2}\omega_{\vec{q}_3 j_3}\omega_{\vec{q}_4 j_4})^{1/2}} (\vec{q}\cdot\vec{\epsilon}_{\vec{q}_1 j_1})(\vec{q}\cdot\vec{\epsilon}_{\vec{q}_2 j_2})(\vec{q}\cdot\vec{\epsilon}^{\,*}_{\vec{q}_3 j_3})(\vec{q}\cdot\vec{\epsilon}^{\,*}_{\vec{q}_4 j_4})$$

$$\times \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}\langle A_{\vec{q}_1 j_1}(t) A_{\vec{q}_2 j_2}(t) A^\dagger_{\vec{q}_3 j_3}(0) A^\dagger_{\vec{q}_4 j_4}(0)\rangle\, dt , \tag{2.35}$$

$$S_4^C(\vec{q},\omega) = -\left(\frac{\hbar}{2NM}\right)^2 \frac{N}{3!} \sum_{\vec{q}_1\vec{q}_2\vec{q}_3 j_1 j_2 j_3 j} \frac{\Delta(\vec{q}-\vec{q}_1-\vec{q}_2-\vec{q}_3)}{(\omega_{\vec{q}_1 j_1}\omega_{\vec{q}_2 j_2}\omega_{\vec{q}_3 j_3}\omega_{\vec{q}j})^{1/2}} (\vec{q}\cdot\vec{\epsilon}_{\vec{q}j})(\vec{q}\cdot\vec{\epsilon}^{\,*}_{\vec{q}_1 j_1})(\vec{q}\cdot\vec{\epsilon}^{\,*}_{\vec{q}_2 j_2})(\vec{q}\cdot\vec{\epsilon}^{\,*}_{\vec{q}_3 j_3})$$

$$\times \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}\langle A_{\vec{q}j}(t) A^\dagger_{\vec{q}_1 j_1}(0) A^\dagger_{\vec{q}_2 j_2}(0) A^\dagger_{\vec{q}_3 j_3}(0)\rangle\, dt . \tag{2.36}$$

The integrals arising in Eqs. (2.34), (2.35), and (2.36) are evaluated from the following respective Green's functions:

$$E_1^A = \langle\langle A_{\vec{q}_1 j_1}(t) A_{\vec{q}_2 j_2}(t) A_{\vec{q}_3 j_3}(t); A^\dagger_{\vec{q}j}(0)\rangle\rangle , \tag{2.37}$$

$$E_1^B = \langle\langle A_{\vec{q}_1 j_1}(t) A_{\vec{q}_2 j_2}(t); A^\dagger_{\vec{q}_3 j_3}(0) A^\dagger_{\vec{q}_4 j_4}(0)\rangle\rangle , \tag{2.38}$$

and

$$E_1^C = \langle\langle A_{\vec{q}j}(t); A^\dagger_{\vec{q}_1 j_1}(0) A^\dagger_{\vec{q}_2 j_2}(0) A^\dagger_{\vec{q}_3 j_3}(0)\rangle\rangle . \tag{2.39}$$

The corresponding expression for $J_4^\alpha(\omega)$ is given by

$$J_4^\alpha(\omega) = -\lim_{\epsilon\to 0} \frac{2}{(1-e^{-\beta\hbar\omega})} \operatorname{Im} E_1^\alpha(\omega+i\epsilon) , \tag{2.40}$$

where α is assigned the value of A, B, and C, respectively.

The derivation of E_1^A requires the solution of eight simultaneous equations involving various Green's functions. In the harmonic approximation the system of equations can be solved exactly to yield

$$E_1^A = \frac{1}{8\pi}\left[(\alpha+\beta+\gamma+\delta)\left(\frac{1}{\omega-\omega_1-\omega_2-\omega_3} - \frac{1}{\omega+\omega_1+\omega_2+\omega_3}\right) + (\alpha+\beta-\gamma-\delta)\left(\frac{1}{\omega-\omega_1-\omega_2+\omega_3} - \frac{1}{\omega+\omega_1+\omega_2-\omega_3}\right)\right.$$

$$+ (\alpha-\beta+\gamma-\delta)\left(\frac{1}{\omega-\omega_1+\omega_2-\omega_3} - \frac{1}{\omega+\omega_1-\omega_2+\omega_3}\right)$$

$$\left. + (\alpha-\beta-\gamma+\delta)\left(\frac{1}{\omega-\omega_1+\omega_2+\omega_3} - \frac{1}{\omega+\omega_1-\omega_2-\omega_3}\right)\right] , \tag{2.41}$$

where

$$\alpha = \delta_{\vec{q}_1\vec{q}}\,\delta_{j_1 j}\,\delta_{\vec{q}_2-\vec{q}_3}\,\delta_{j_2 j_3} N_{\vec{q}_2 j_2} , \quad \beta = \delta_{\vec{q}_2\vec{q}}\,\delta_{j_2 j}\,\delta_{\vec{q}_3-\vec{q}_1}\,\delta_{j_3 j_1} N_{\vec{q}_3 j_3} ,$$

$$\gamma = \delta_{\vec{q}_3\vec{q}}\,\delta_{j_3 j}\,\delta_{\vec{q}_1-\vec{q}_2}\,\delta_{j_1 j_2} N_{\vec{q}_1 j_1} , \quad \delta = -\left(\frac{\omega_2}{\omega_3}\alpha + \frac{\omega_3}{\omega_1}\beta + \frac{\omega_1}{\omega_2}\gamma\right) ,$$

and

$$\omega_{\vec{q}_i j_i} = \omega_i , \quad i = 1, 2, 3 .$$

The derivation of E_1^B requires the solution of four simultaneous equations involving various Green's functions. Once again, in the harmonic approximation, an exact solution can be found, viz.,

$$E_1^B = \frac{1}{2\pi} F(\vec{q}_1 j_1, \vec{q}_2 j_2; \omega)(\delta_{\vec{q}_3\vec{q}_1}\,\delta_{j_3 j_1}\,\delta_{\vec{q}_4\vec{q}_2}\,\delta_{j_4 j_2} + \delta_{\vec{q}_4\vec{q}_1}\,\delta_{j_4 j_1}\,\delta_{\vec{q}_3\vec{q}_2}\,\delta_{j_3 j_2}) , \tag{2.42}$$

where the function $F(\vec{q}_1 j_1, \vec{q}_2 j_2; \omega)$ is given by Eq. (2.17d).

The Green's function E_1^C involves only one operator at time t and hence will be a function of only one frequency $\omega_{\vec{q}j}$, viz.,

$$E_1^C = \frac{\omega_{\vec{q}j}}{\pi} \frac{(\alpha+\beta+\gamma)}{(\omega^2-\omega_{\vec{q}j}^2)}, \tag{2.43}$$

where the factors α, β, and γ involving sums and products of Kronecker deltas have been defined in Eq. (2.41). The final expressions for $S_4^\alpha(\vec{q}, \omega)$ are obtained by evaluating $J_4^\alpha(\omega)$ [Eq. (2.40)] for each of the three Green's functions given by Eqs. (2.41) to (2.43).

The results are then substituted in the corresponding $S_4^\alpha(\vec{q}, \omega)$ given by Eqs. (2.34) to (2.36). We find

$$S_4^A(\vec{q}, \omega) = -\left(\frac{\hbar}{2NM}\right)^2 \frac{3N}{3!} \sum_{\vec{q}_1 j_1 j} \frac{|\vec{q}\cdot\vec{\epsilon}_{\vec{q}j}|^2 |\vec{q}\cdot\vec{\epsilon}_{\vec{q}_1\vec{q}_1}|^2}{\omega_{\vec{q}j}\omega_{\vec{q}_1 j_1}} N_{\vec{q}_1 j_1} \frac{1}{(1-e^{-\beta\hbar\omega})} [\delta(\omega-\omega_{\vec{q}j}) - \delta(\omega+\omega_{\vec{q}j})], \tag{2.44}$$

$$S_4^B(\vec{q}, \omega) = \left(\frac{\hbar}{2NM}\right)^2 \frac{N}{(2!)^2} \sum_{\vec{q}_1\vec{q}_2 j_1 j_2} \Delta(-\vec{q}+\vec{q}_1+\vec{q}_2) \frac{|\vec{q}\cdot\vec{\epsilon}_{\vec{q}_1 j_1}|^2 |\vec{q}\cdot\vec{\epsilon}_{\vec{q}_2 j_2}|^2}{\omega_{\vec{q}_1 j_1}\omega_{\vec{q}_2 j_2}} \frac{1}{(1-e^{-\beta\hbar\omega})} 2G(\vec{q}_1 j_1, \vec{q}_2 j_2; \omega), \tag{2.45}$$

where $G(\vec{q}_1 j_1, \vec{q}_2 j_2; \omega)$ has been defined in Eq. (2.18b) and

$$S_4^C(\vec{q}, \omega) = S_4^A(\vec{q}, \omega). \tag{2.46}$$

III. CALCULATION OF RESISTIVITY FROM $S(\vec{q},\omega)$

From expansion (2.6) of $S(\vec{q}, \omega)$ and expression (1.2) for ρ, we find

$$\rho = \rho_2(T) + \rho_3(T) + \rho_4(T) + \cdots, \tag{3.1}$$

where $\rho_2(T)$, $\rho_3(T)$, and $\rho_4(T)$ are considered separately and represent the contributions from $S_2(\vec{q}, \omega)$, $S_3(\vec{q}, \omega)$, and $S_4(\vec{q}, \omega)$, respectively.

A. Calculation of $\rho_2(T)$

The expression of $\rho_2(T)$ is given by

$$\rho_2(T) = C \int_{<2k_F} d\vec{q}\, q\, |W(q)|^2 \int_{-\infty}^{+\infty} d\omega \frac{\beta\omega}{(e^{\beta\hbar\omega}-1)} S_2(\vec{q}, \omega). \tag{3.2}$$

Substituting for $S_2(\vec{q}, \omega)$ from Eqs. (2.12) and (2.15), we obtain

$$\rho_2(T) = \frac{C\hbar}{\pi M} \sum_j \int_{<2k_F} d\vec{q}\, q\, |W(q)|^2 |\vec{q}\cdot\vec{\epsilon}_{\vec{q}j}|^2 \times \int_{-\infty}^{+\infty} d\omega \frac{\beta\omega}{(e^{\beta\hbar\omega}-1)(1-e^{-\beta\hbar\omega})} \times \left(\frac{2\omega_{\vec{q}j}\Gamma_{\vec{q}j}(\omega)}{(\omega^2-\Omega_{\vec{q}j}^2)^2 + 4\omega_{\vec{q}j}^2\Gamma_{\vec{q}j}^2(\omega)}\right). \tag{3.3}$$

The last integral over ω in Eq. (3.3) can be approximated as follows:

$$Z[\omega, \Omega_{\vec{q}j}(\omega), \Gamma_{\vec{q}j}(\omega)] = \frac{2\omega_{\vec{q}j}\Gamma_{\vec{q}j}(\omega)}{(\omega^2-\Omega_{\vec{q}j}^2)^2 + 4\omega_{\vec{q}j}^2\Gamma_{\vec{q}j}^2(\omega)}. \tag{3.4}$$

The function Z peaks in the regions $\omega = \pm\Omega_{\vec{q}j}$, and since the width $\Gamma_{\vec{q}j}(\omega)$ is small, it can therefore be expanded about any point in the neighborhood of $\Gamma_{\vec{q}j}(\omega) = 0$. One common approximation is to replace this function Z by the delta function $\pi\delta(\omega^2-\Omega_{\vec{q}j}^2)$, which corresponds to the first term in the MacLaurin's expansion. When the integral given by Eq. (3.3) is evaluated in this approximation, we obtain Eq. (1.1) with $f(\beta\omega_{\vec{q}j})$ replaced by $f(\beta\Omega_{\vec{q}j})$ in Eq. (1.1b).

The above approximation yields only one of the contributions to $\rho(T)$ of $O(\lambda^2)$. The other is obtained from the next term in the MacLaurin's expansion of Z, viz,

$$Z = \pi\delta(\omega^2-\Omega_{\vec{q}j}^2) + \frac{2\omega_{\vec{q}j}\Gamma_{\vec{q}j}(\omega)}{(\omega^2-\omega_{\vec{q}j}^2)^2} + \cdots. \tag{3.5}$$

When the integral in Eq. (3.3) is evaluated with the second term in Eq. (3.5), we obtain the following explicit contribution to $\rho(T)$ from the phonon width, viz.,

$$\rho_2^W(T) = \frac{C\hbar}{\pi M} \sum_j \int_{<2k_F} d\vec{q}\, q\, |W(q)|^2 |\vec{q}\cdot\vec{\epsilon}_{\vec{q}j}|^2 I(\vec{q}j)\omega(\vec{q}j), \tag{3.6}$$

where

$$I(\vec{q}j)=\frac{18\pi\lambda^2\beta}{\hbar^2}\sum_{\vec{q}_1j_1\vec{q}_2j_2}|V^3(-\vec{q}j,\vec{q}_1j_1,\vec{q}_2j_2)|^2\left((N_{\vec{q}_1j_1}+N_{\vec{q}_2j_2})\frac{(\omega_{\vec{q}_1j_1}+\omega_{\vec{q}_2j_2})}{[\cosh\beta\hbar(\omega_{\vec{q}_1j_1}+\omega_{\vec{q}_2j_2})-1]}\frac{1}{[(\omega_{\vec{q}_1j_1}+\omega_{\vec{q}_2j_2})^2-\omega_{\vec{q}j}^2]^2}\right.$$
$$\left.+(N_{\vec{q}_2j_2}-N_{\vec{q}_1j_1})\frac{(\omega_{\vec{q}_1j_1}-\omega_{\vec{q}_2j_2})}{[\cosh\beta\hbar(\omega_{\vec{q}_1j_1}-\omega_{\vec{q}_2j_2})-1]}\frac{1}{[(\omega_{\vec{q}_1j_1}-\omega_{\vec{q}_2j_2})^2-\omega_{\vec{q}j}^2]^2}\right). \quad (3.7)$$

We note that $\Omega_{\vec{q}j}$ in the function $f(\beta\Omega_{\vec{q}j})$, as given by Eq. (2.16), is well approximated by

$$\Omega_{\vec{q}j}=\omega_{\vec{q}j}+\Delta_{\vec{q}j}(\omega_{\vec{q}j}), \quad (3.8)$$

where the phonon shift $\Delta_{\vec{q}j}(\omega)$ defined by Eq. (2.17a) is evaluated at $\omega=\omega_{\vec{q}j}$.

Substituting for $\Omega_{\vec{q}j}$ from Eq. (3.8) into $f(\beta\Omega_{\vec{q}j})$, expanding in powers of $\Delta_{\vec{q}j}(\omega_{\vec{q}j})$, and retaining only the linear term in $\Delta_{\vec{q}j}(\omega_{\vec{q}j})$, as it is of $O(\lambda^2)$, we obtain

$$f(\beta\Omega_{\vec{q}j})=f(\beta\omega_{\vec{q}j})-\left(\frac{\beta\hbar}{4}\right)\Delta_{\vec{q}j}(\omega_{\vec{q}j})\frac{\coth(\frac{1}{2}\beta\hbar\omega_{\vec{q}j})}{\sinh^2(\frac{1}{2}\beta\hbar\omega_{\vec{q}j})}. \quad (3.9)$$

It is clear that, when Eq. (3.9) is substituted into Eq. (1.1), we get formally the following contributions to $\rho_2(T)$:

$$\rho_2^H(T)+\rho_2^C(T)+\rho_2^Q(T),$$

where $\rho_2^H(T)$ is the usual harmonic contribution to $\rho(T)$. $\rho_2^C(T)$ and $\rho_2^Q(T)$ are the contributions from the cubic and quartic phonon frequency shifts. Full expressions for $\rho_2^C(T)$ and $\rho_2^Q(T)$ are given by

$$\rho_2^*(T)=\frac{C\hbar}{M}\sum_j\int_{<2k_F}d\vec{q}\,q\,|W(q)|^2\beta|\vec{q}\cdot\vec{\epsilon}_{\vec{q}j}|^2\times\left(-\frac{\beta\hbar}{4}\right)\Delta_{\vec{q}j}^*(\omega_{\vec{q}j})\frac{\coth(\frac{1}{2}\beta\hbar\omega_{\vec{q}j})}{\sinh^2(\frac{1}{2}\beta\hbar\omega_{\vec{q}j})}, \quad (3.10)$$

where $*=C$ or Q, and the quantities $\Delta_{\vec{q}j}^C(\omega_{\vec{q}j})$ and $\Delta_{\vec{q}j}^Q(\omega_{\vec{q}j})$ are defined in Eqs. (2.17b) and (2.17c), respectively.

B. Calculation of $\rho_3(T)$

The contribution to $\rho(T)$ from $S_3(\vec{q},\omega)$, viz., $\rho_3(T)$ is obtained from $S_3^A(\vec{q},\omega)$ and $S_3^B(\vec{q},\omega)$. Since $S_2^B(\vec{q},\omega)=-S_3^A(-\vec{q},\omega)$ as shown in Sec. II, we obtain from Eqs. (2.33) and (1.2) and the arguments presented in Sec. II,

$$\rho_3(T)=C\int_{<2k_F}d\vec{q}\,q\,|W(q)|^2(-i)\left(\frac{\hbar}{2MN}\right)^{3/2}\left(\frac{2N}{2!}\right)\sum_{\vec{q}_1\vec{q}_2j_1j_2j}\Delta(\vec{q}-\vec{q}_1-\vec{q}_2)\frac{(\vec{q}\cdot\vec{\epsilon}^{\,*}_{\vec{q}j})(\vec{q}\cdot\vec{\epsilon}_{\vec{q}_1j_1})(\vec{q}\cdot\vec{\epsilon}_{\vec{q}_2j_2})}{(\omega_{\vec{q}j}\omega_{\vec{q}_1j_1}\omega_{\vec{q}_2j_2})^{1/2}}\times\int_{-\infty}^{+\infty}\frac{\beta\omega}{(e^{\beta\hbar\omega}-1)}J_3^A(\omega)\,d\omega. \quad (3.11)$$

The last integral, although tedious, can be evaluated from Eqs. (2.23), (2.24), and (2.17d). In compact notation, the integral is given by

$$\int_{-\infty}^{+\infty}d\omega\frac{\beta\omega}{(e^{\beta\hbar\omega}-1)}J_3^A(\omega)d\omega=\frac{\lambda}{\hbar}V^3(-\vec{q}_1j_1,-\vec{q}_2j_2,\vec{q}j)$$
$$\times 12\beta\omega_{\vec{q}j}\left[\frac{(N_{\vec{q}_1j_1}+N_{\vec{q}_2j_2})(\omega_{\vec{q}_1j_1}+\omega_{\vec{q}_2j_2})}{(\omega_{\vec{q}_1j_1}+\omega_{\vec{q}_2j_2})^2-\omega_{\vec{q}j}^2}[\operatorname{cosech}^2\beta\hbar\tfrac{1}{2}(\omega_{\vec{q}_1j_1}+\omega_{\vec{q}_2j_2})-\operatorname{cosech}^2\tfrac{1}{2}\beta\hbar\omega_{\vec{q}j}]\right.$$
$$\left.+\frac{(N_{\vec{q}_1j_1}-N_{\vec{q}_2j_2})(\omega_{\vec{q}_1j_1}-\omega_{\vec{q}_2j_2})}{(\omega_{\vec{q}_1j_1}-\omega_{\vec{q}_2j_2})^2-\omega_{\vec{q}j}^2}[\operatorname{cosech}^2\beta\hbar\tfrac{1}{2}(\omega_{\vec{q}_1j_1}-\omega_{\vec{q}_2j_2})-\operatorname{cosech}^2\tfrac{1}{2}\beta\hbar\omega_{\vec{q}j}]\right]. \quad (3.12)$$

C. Calculation of $\rho_4(T)$

Since we have shown in Sec. II the equivalence of $S_4^A(\vec{q},\omega)$ and $S_4^C(\vec{q},\omega)$, there are only two distinct contributions to $\rho(T)$ arising from $S_4^A(\vec{q},\omega)$ and $S_4^B(\vec{q},\omega)$. Substituting the expressions for $S_4^A(\vec{q},\omega)$ and $S_4^B(\vec{q},\omega)$ given by Eqs. (2.44) and (2.45), respectively, into Eq. (1.2) and integrating over ω, we obtain

$$\rho_4^x(T)=C\int_{<2k_F} d^3\vec{q}\, q\,|W(q)|^2 I_4^x(\vec{q}) , \tag{3.13}$$

where $x=A$ or B, and

$$I_4^A(\vec{q})=-\frac{\hbar}{2NM}\sum_j \frac{6N}{3!}|\vec{q}\cdot\epsilon_{\vec{q}j}|^2\beta f(\beta\omega_{\vec{q}j})D(\vec{q}) , \tag{3.14a}$$

$$D(\vec{q})=\frac{\hbar}{2NM}\sum_{\vec{q}_1j_1}\frac{|\vec{q}\cdot\epsilon_{\vec{q}_1j_1}|^2}{\omega_{\vec{q}_1j_1}}N_{\vec{q}_1j_1} , \tag{3.14b}$$

$$I_4^B(\vec{q})=\left(\frac{\hbar}{2NM}\right)^2\frac{N}{(2!)^2}\sum_{\vec{q}_1j_1\vec{q}_2j_2}\Delta(-\vec{q}+\vec{q}_1+\vec{q}_2)\frac{|\vec{q}\cdot\epsilon_{\vec{q}_1j_1}|^2|\vec{q}\cdot\epsilon_{\vec{q}_2j_2}|^2}{\omega_{\vec{q}_1j_1}\omega_{\vec{q}_2j_2}}\frac{\beta}{4}H(\vec{q}_1j_1,\vec{q}_2j_2) , \tag{3.15a}$$

$$\begin{aligned}H(\vec{q}_1j_1,\vec{q}_2j_2)=&(N_{\vec{q}_1j_1}+N_{\vec{q}_2j_2})(\omega_{\vec{q}_1j_1}+\omega_{\vec{q}_2j_2})\operatorname{cosech}^2\tfrac{1}{2}\beta\hbar(\omega_{\vec{q}_1j_1}+\omega_{\vec{q}_2j_2})\\&+(N_{\vec{q}_2j_2}-N_{\vec{q}_1j_1})(\omega_{\vec{q}_1j_1}-\omega_{\vec{q}_2j_2})\operatorname{cosech}^2\tfrac{1}{2}\beta\hbar(\omega_{\vec{q}_1j_1}-\omega_{\vec{q}_2j_2}) ,\end{aligned} \tag{3.15b}$$

and the function $f(\omega_{\vec{q}j})$ arising in Eq. (3.14a) was defined earlier in Eq. (1.1b).

IV. HIGH-TEMPERATURE LIMIT OF $\rho(T)$

In the high-temperature limit, i.e., $T>\theta_D$, the Debye temperature, it is possible to expand in powers of T the thermal factors arising in the expressions of $\rho_2(T)$, $\rho_3(T)$, and $\rho_4(T)$ derived in Sec. III. $\rho_2(T)$ contains four terms arising from the harmonic, cubic and quartic shifts, and the phonon width. In the high-temperature limit the harmonic contribution is proportional to T and the contributions from the cubic and quartic shifts and the phonon width are all proportional to T^2. We can summarize all the leading high-temperature-limit contributions to $\rho_2(T)$ in the following equation:

$$\rho_2(T)=(\rho_2)_H T+(\rho_2)_C T^2+(\rho_2)_Q T^2+(\rho_2)_W T^2 , \tag{4.1}$$

where all the coefficients of T and T^2 in Eq. (4.1) are independent of T. $(\rho_2)_H$ is obtained from Eqs. (1.1a) and (1.1b). $(\rho_2)_C$, $(\rho_2)_Q$, and $(\rho_2)_W$ are of $O(\lambda^2)$. $(\rho_2)_W$ is obtained from Eqs. (3.6) and (3.7), while $(\rho_2)_C$ and $(\rho_2)_Q$ are obtained from Eqs. (3.10), (2.17b), and (2.17c).

In the high-temperature limit, $\rho_3(T)$ can be expanded in powers of T and the leading contribution is of the order T^2. From Eqs. (3.11) and (3.12), we have

$$\rho_3(T)=(\rho_3)_I T^2 . \tag{4.2}$$

We note that $\rho_3(T)$ is of $O(\lambda)$ and arises from the cubic term in the Taylor expansion of the crystal potential energy.

The remaining high-temperature-limit contributions of $O(T^2)$ to $\rho(T)$ from the Debye-Waller factor and the first term of the multiphonon series are obtained from $\rho_4^A(T)$ and $\rho_4^B(T)$, respectively. Although these terms are of $O(T^2)$, they are essentially harmonic in nature and therefore independent of the parameter λ. From Eqs. (3.13) to (3.15) we find

$$\rho_4(T)=(\rho_4)_{\rm DW}T^2+(\rho_4)_{\rm mp}T^2 . \tag{4.3}$$

It is straightforward to obtain the temperature-independent coefficients in Eqs. (4.1) to (4.3) from the respective equations derived in Sec. III.

V. DISCUSSION

We have evaluated the contributions to the phonon-limited resistivity, (ρ) of metals from the anharmonicity, the Debye-Waller factor and the first term of the multiphonon series. The latter two contributions to ρ are obtained from the correlation functions involving four operators, whereas the anharmonic contributions arise from the two- and three-operator correlation functions. The three-operator correlation function represents an explicit anharmonic contribution to ρ from the cubic term of the Taylor expansion of the crystal potential energy. The other anharmonic contributions to ρ from the cubic and quartic shift of phonon frequencies and the phonon width and are obtained from the two-operator correlation functions.

The correlation functions are evaluated exactly from the respective Green's functions. The mathematical structure of the contributions to ρ from the cubic shift, phonon width, the three-operator correlation function, and the first term of the multiphonon series have one thing in common, viz., the delta function $\Delta(\vec{q}+\vec{q}_1+\vec{q}_2)$, restricting the three wave vectors.

In the high-temperature limit ($T>\theta_D$) all the above contributions to ρ are found to vary as T^2. The higher-order correlation functions (viz., five- and six-operator, etc.) yield a higher-order temperature dependence (T^3, etc.) in the high-temperature limit. Similarly, the anharmonic terms of $O(\lambda^2)$ in the evaluation of four-operator correlation functions and terms of $O(\lambda^4)$ in the evaluation of two-operator correlation functions produce a higher-order term in ρ in the high-temperature limit (i.e., T^3, etc.).

The same argument holds true in the case of three-operator correlation functions. Thus our theory of the phonon-limited resistivity presented in this paper omits these higher-order terms.

Finally, we make some remarks about the decoupling procedure in obtaining the Green's function and the correlation function. The two-operator Green's function has been obtained exactly to $O(\lambda^2)$. The details of the derivation, which requires some decoupling procedure, have been given in Ref. 6. The other Green's functions involving three and four operators can be obtained exactly, and no decoupling procedure is needed in their derivation. However, if the Green's functions E_1^A and E_1^C are obtained by decoupling, we find

$$E_1^A=3\langle A_{\vec{q}_2j_2}(t)A_{\vec{q}_3j_3}(t)\rangle\langle\langle A_{\vec{q}_1j_1}(t);A^\dagger_{\vec{q}j}(0)\rangle\rangle\,, \qquad (5.1)$$

$$E_1^C=3\langle A^\dagger_{\vec{q}_2j_2}(0)A^\dagger_{\vec{q}_3j_3}(0)\rangle\langle\langle A_{\vec{q}j}(t);\ A^\dagger_{\vec{q}_1j_1}(0)\rangle\rangle\,. \qquad (5.2)$$

Since in the harmonic approximation

$$\langle A_{\vec{q}_2j_2}(t)A_{\vec{q}_3j_3}(t)\rangle=\langle A^\dagger_{\vec{q}_2j_2}(0)A^\dagger_{\vec{q}_3j_3}(0)\rangle = N_{\vec{q}_2j_2}\delta_{\vec{q}_2\vec{q}_3}\delta_{j_2j_3}\,, \qquad (5.3)$$

the corresponding S_4^A obtained from Eqs. (5.1) and (5.2) is the same as that given by Eq. (2.44). In this case then the decoupling procedure gives the same result for S_4^A, as obtained from the exact Green's function, viz, Eq. (2.44), and of course we find $S_4^A=S_4^C$. No decoupling procedure can be applied to obtain E_1^B. However, the correlation function arising in the integrand in S_4^B given by Eq. (2.35) can be decoupled to give

$$\begin{aligned}\langle A_{\vec{q}_1j_1}(t)A_{\vec{q}_2j_2}(t)A^\dagger_{\vec{q}_3j_3}(0)A^\dagger_{\vec{q}_4j_4}(0)\rangle &=\langle A_{\vec{q}_1j_1}(t)A_{\vec{q}_2j_2}(t)\rangle\langle A^\dagger_{\vec{q}_3j_3}(0)A^\dagger_{\vec{q}_4j_4}(0)\rangle\\ &+\langle A_{\vec{q}_1j_1}(t)A^\dagger_{\vec{q}_3j_3}(0)\rangle\langle A_{\vec{q}_2j_2}(t)A^\dagger_{\vec{q}_4j_4}(0)\rangle\\ &+\langle A_{\vec{q}_1j_1}(t)A^\dagger_{\vec{q}_4j_4}(0)\rangle\langle A_{\vec{q}_2j_2}(t)A^\dagger_{\vec{q}_3j_3}(0)\rangle\,. \end{aligned} \qquad (5.4)$$

The first term in Eq. (5.4) is independent of time, as seen from Eq. (5.3). This term does not contribute in the derivation of ρ_4^B. The second and third terms in Eq. (5.4) make equal contributions in the evaluation of ρ_4^B. These contributions can be evaluated in the harmonic approximation. The time-dependent correlation function is given by

$$\langle A_{\vec{q}_1j_1}(t)A^\dagger_{\vec{q}_3j_3}(0)\rangle=\int_{-\infty}^{+\infty}e^{-i\omega t}\,J_{\vec{q}_1j_1j_3}(\omega)\delta_{\vec{q}_1\vec{q}_3}\,d\omega\,,$$

where $J_{q_1j_1j_3}$ was defined earlier in Eq. (2.13). We omit the details here but simply note that ρ_4^B obtained by this procedure is identical to the ρ_4^B obtained exactly and given by Eq. (3.13).

VI. CONCLUSION

All the contributions to the phonon-limited resistivity of metals which are found to vary as T^2 in the high-temperature limit have been derived. The expressions for the various contributions to ρ (six of them), which have been derived from the appropriate Green's functions, are valid for all temperatures. The physical significance of these contributions has been demonstrated.

The results of a detailed first-principles numerical computation[12] of these six contributions to the coefficient B in the BT^2 term in ρ in Na and K show a strong pairwise cancellation among the following contributions to ρ: Debye-Waller factor and multiphonon term, cubic and quartic phonon shift, phonon width, and interference term. Very recently, these numerical results for K have been used by Cook *et al.*[13] in the estimation of the vacancy formation energy from the high-temperature resistivity measurements. A manuscript containing these Na and K numerical results[12] is in preparation.

ACKNOWLEDGMENT

This work was supported by the Natural Sciences and Engineering Research Council of Canada.

---

[1]G. Baym, Phys. Rev. 135, A1691 (1964).
[2]M. P. Greene and W. Kohn, Phys. Rev. 137, A513 (1965).
[3]G. Grimvall, Phys. Cond. Matter 17, 135 (1974).
[4]R. C. Shukla and R. Taylor, J. Phys. F 6, 531 (1976).
[5]R. C. Shukla, E. R. Muller, M. VanderSchans, Thermal Conductivity 15, 191 (1978).
[6]R. C. Shukla and E. R. Muller, Phys. Status Solidi B

43, 413 (1971).
[7]M. Born and K. Huang, *The Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954).
[8]R. C. Shukla and E. R. Muller, Phys. Status Solidi 39, 561 (1970).
[9]D. N. Zubarev, Usp. Fiz. Nauk 71, 71 (1960) [Sov. Phys.—Usp. 3, 320 (1960)].
[10]R. C. Dynes and J. P. Carbotte, Phys. Rev. 175, 913 (1968).
[11]N. H. March, W. M. Young, S. Sampanthar, *The Many-Body Problem in Quantum Mechanics* (Cambridge, England, 1967), p. 276.
[12]R. C. Shukla and M. VanderSchans (unpublished).
[13]J. G. Cook, Roger Taylor, and M. J. Laubitz, J. Phys. F 9, 1503 (1979).