Thermal conductivity and shear viscosity of anharmonic doped crystals: An improved fundamental approach

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In real crystals at finite temperature there exist some impurities and anharmonic effects invariably. These effects are studied here with use of the Green-function method as formulated by Zubarev. The calculations are restricted to the Brevais lattice for simplicity. New expressions for the lattice thermal conductivity and shear viscosity are derived for such crystals.

I. INTRODUCTION

Various properties of a crystal, like thermal conductivity, thermal expansion, shear viscosity, variations of elastic constants, etc., are caused by the modification of the perfect motion of phonons in the crystal. One possible reason for this modification is the presence of impurities. The study of thermal conductivity in solids doped with impurities has received much attention. However, most of the attempts are phenomenological in nature, starting from modifications of Callaway's expression for the thermal conductivity.[1–7]

Recently the thermal conductivity in crystals with substitutional defects has been investigated[8] using a more fundamental approach based on the correlation function formalism of Kubo.[9] A powerful method is to use the double-time thermal Green-function technique as formulated by Zubarev,[10] and further developed by Mavroyannis[11] and Mahanty.[12] However, if the double-time Green functions are evaluated by the help of the Dyson equation, one is left with an unsolved integral over frequency.[8]

In Ref. 8 the equation of motion for the Green function $G_{kk'}(\omega)$ is written in the form of the Dyson equation

$$G_{kk'}(\omega)=G_k^0(\omega)\delta_{kk'}+G_k^0(\omega)\widetilde{P}_{kk'}^{(1)}(\omega)G_{k'}^0(\omega) \ . \tag{1}$$

The polarization operator $\Pi_{kk'}(\omega)$ is defined by

$$G_{kk'}(\omega)=G_k^0(\omega)\delta_{kk'}+G_k^0(\omega)\Pi_{kk'}(\omega)G_{kk'}(\omega) \tag{2}$$

so that

$$G_{kk'}(\omega)=G_k^0(\omega)\delta_{kk'}/[1-G_k^0(\omega)\Pi_{kk'}(\omega)] \ . \tag{3}$$

This step is not valid in general, as it implies that $G_{kk'}(\omega)$ vanishes for $k\neq k'$. It has been approximated[8] by putting $\Pi_{kk}(\omega)\equiv\Pi_k(\omega)$ and

$$G_{kk'}(\omega)=\frac{\delta_{kk'}}{[G_k^0(\omega)]^{-1}-\Pi_k(\omega)} \tag{4}$$

together with

$$\Pi_k(\omega)=\widetilde{P}_{kk}^{(1)}(\omega)/[1+G_k^0(\omega)\widetilde{P}_{kk}^{(1)}(\omega)] \ . \tag{5}$$

Thus the nondiagonal terms are completely ignored and the integration over ω remains until the end.

We proceed in this paper by a simple perturbation expansion up to the second-order terms which does not involve these approximations as far as it goes. Every Green function can be expressed as a perturbation series in zeroth-order Green functions of the form

$$G(\omega)=\sum_{k_1}a_{k_1}G_{k_1}^0(\omega)+\sum_{k_2}b_{k_2}\overline{G}\,{}_{k_2}^0(\omega) \ , \tag{6}$$

where

$$G_{k_1}^0(\omega)=\frac{\omega_{k_1}}{\pi\hbar(\omega^2-\omega_{k_1}^2)}$$

and

$$\overline{G}\,{}_{k_2}^0(\omega)=\frac{\omega}{\pi\hbar(\omega^2-\omega_{k_2}^2)} \ . \tag{7}$$

Decomposing into partial functions

$$G_{k_1}^0(\omega)=\frac{1}{2\pi\hbar}\left[\frac{1}{\omega-\omega_{k_1}}-\frac{1}{\omega+\omega_{k_1}}\right] ,$$

$$\overline{G}\,{}_{k_2}^0(\omega)=\frac{1}{2\pi\hbar}\left[\frac{1}{\omega-\omega_{k_2}}+\frac{1}{\omega+\omega_{k_2}}\right] , \tag{8}$$

we can write the corresponding spectral density functions,

$$J_{k_1}(\omega)=\frac{-2\,\mathrm{Im}G_{k_1}(\omega)}{e^{\beta\hbar\omega}-1}=\frac{\delta(\omega-\omega_{k_1})-\delta(\omega+\omega_{k_1})}{e^{\beta\hbar\omega}-1} ,$$

$$\overline{J}_{k_2}(\omega)=\frac{-2\,\mathrm{Im}\overline{G}_{k_2}(\omega)}{e^{\beta\hbar\omega}-1}=\frac{\delta(\omega-\omega_{k_2})+\delta(\omega+\omega_{k_2})}{e^{\beta\hbar\omega}-1} \ . \tag{9}$$

After decoupling and expanding in terms of zeroth-order Green functions, we get terms of the form

$$\lim_{\epsilon\to 0}\text{Re}\int_0^\infty dt\, e^{-\epsilon t}\int_{-\infty}^{\infty} d\omega\, J_{k_1}(\omega)e^{\beta\hbar\omega}e^{i\hbar\omega t}\int_{-\infty}^{\infty} d\omega'\, J_{k_2}(\omega')e^{\beta\hbar\omega'}e^{i\hbar\omega' t}=\pi\int_{-\infty}^{\infty} d\omega\, J_{k_1}(\omega)J_{k_2}(-\omega)=\frac{2\pi e^{\beta\hbar\omega_{k_1}}}{(e^{\beta\hbar\omega_{k_1}}-1)^2}\delta_{\omega_{k_1}\omega_{k_2}},$$

$$\lim_{\epsilon\to 0}\text{Re}\int_0^\infty dt\, e^{-\epsilon t}\int_{-\infty}^{\infty} d\omega\, \bar{J}_{k_1}(\omega)e^{\beta\hbar\omega}e^{i\hbar\omega t}\int_{-\infty}^{\infty} d\omega'\, \bar{J}_{k_2}(\omega')e^{\beta\hbar\omega'}e^{i\hbar\omega' t}=\frac{-2\pi e^{\beta\hbar\omega_{k_1}}}{(e^{\beta\hbar\omega_{k_1}}-1)^2}\delta_{\omega_{k_1}\omega_{k_2}}, \tag{10}$$

$$\lim_{\epsilon\to 0}\text{Re}\int_0^\infty dt\, e^{-\epsilon t}\int_{-\infty}^{\infty} d\omega\, J_{k_1}(\omega)e^{\beta\hbar\omega}e^{i\hbar\omega t}\int_{-\infty}^{\infty} d\omega'\, \bar{J}_{k_2}(\omega')e^{\beta\hbar\omega'}e^{i\hbar\omega' t}$$
$$=\lim_{\epsilon\to 0}\text{Re}\int_0^\infty dt\, e^{-\epsilon t}\int_{-\infty}^{\infty} d\omega\, \bar{J}_{k_1}(\omega)e^{\beta\hbar\omega}e^{i\hbar\omega t}\int_{-\infty}^{\infty} d\omega'\, J_{k_2}(\omega')e^{\beta\hbar\omega'}e^{i\hbar\omega' t}=0\ .$$

Using these results we can calculate the various terms in the expansion of the thermal conductivity. Note that the final result, unlike Ref. 8, does not involve any unresolved integral over ω. We also apply our method to shear viscosity. We consider phonon-phonon interactions caused by the lattice anharmonicity and isotropic mass defects whose concentration is small, making the impurity-impurity interaction negligible.

II. HAMILTONIAN FOR THE ANHARMONIC DOPED CRYSTAL

In second quantization, the Hamiltonian for an anharmonic crystal, with a low concentration of impurities, has the form

$$H=H_0+H_1,\quad H_1=H_d+H_a\ , \tag{11}$$

where

$$H_0=\sum_k \hbar\omega_k(a_k^\dagger a_k+\tfrac{1}{2})=\tfrac{1}{4}\sum_k \hbar\omega_k(A_k^\dagger A_k+B_k^\dagger B_k)\ , \tag{12}$$

$$H_d=\sum_{k_1,k_2}\hbar D(k_1,k_2)A_{k_1}A_{k_2}-\sum_{k_1,k_2}\hbar C(k_1,k_2)B_{k_1}B_{k_2}\ , \tag{13}$$

$$H_a=\sum_{n=3}^{\infty}\sum_{k_1,\ldots,k_n}\hbar V_n(k_1,\ldots,k_n)A_{k_1}\times\cdots\times A_{k_n}\ . \tag{14}$$

H_0 is the harmonic Hamiltonian for the perfect lattice, H_d is the change in the harmonic Hamiltonian due to impurities, and H_a is the anharmonic part of the Hamiltonian. For brevity we have written k here for $\mathbf{k},s$, where $\mathbf{k}$ is the wave vector and s the polarization of the phonon whose annihilation and creation operators are $a_{\mathbf{k}s}$ and $a_{\mathbf{k}s}^\dagger$ with

$$A_{\mathbf{k}s}=a_{\mathbf{k}s}+a_{-\mathbf{k}s}^\dagger,\quad B_{\mathbf{k}s}=a_{\mathbf{k}s}-a_{-\mathbf{k}s}^\dagger\ . \tag{15}$$

The displacement of the atom at lattice site $\mathbf{r}_i$ is

$$\mathbf{u}_i=\left[\frac{\hbar}{2M_0N}\right]^{1/2}\sum_{\mathbf{k},s}\epsilon_{\mathbf{k}s}\omega_{\mathbf{k}s}^{-1/2}A_{\mathbf{k}s}e^{i\mathbf{k}\cdot\mathbf{r}_i}\ , \tag{16}$$

where

$$\frac{1}{M_0}=\frac{f}{M'}+\frac{1-f}{M}\ , \tag{17}$$

with $\epsilon_{\mathbf{k}s}$ the unit vector for the sth polarization component on the mode $\mathbf{k}$, M the mass of the host atom, M' the mass of the substitutional impurity, N the number of host atoms, and f the impurity concentration. For simplicity, we treat the Brevais lattice only. The coefficients C and D in H_d have the form

$$C(k_1,k_2)=C(\mathbf{k}_1,s_1;\mathbf{k}_2,s_2)$$
$$=\frac{M_0}{4\mu N}(\omega_{\mathbf{k}_1s_1}\omega_{\mathbf{k}_2s_2})^{1/2}\epsilon_{\mathbf{k}_1s_1}\cdot\epsilon_{\mathbf{k}_2s_2}\left[f\sum_{j=1}^{N}e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{r}_j}-\sum_{i=1}^{n}e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{r}_i}\right]\ , \tag{18}$$

$$D(k_1,k_2)=D(\mathbf{k}_1,s_1;\mathbf{k}_2,s_2)$$
$$=\frac{1}{4NM_0}\sum_{i,j}\sum_{\alpha,\beta}(\omega_{\mathbf{k}_1s_1}\omega_{\mathbf{k}_2s_2})^{1/2}\Delta\Phi_{\alpha\beta}(\mathbf{r}_i,\mathbf{r}_j)\epsilon_{\mathbf{k}_1s_1}^{\alpha}\epsilon_{\mathbf{k}_2s_2}^{\beta}e^{i(\mathbf{k}_1\cdot\mathbf{r}_i+\mathbf{k}_2\cdot\mathbf{r}_j)}\ , \tag{19}$$

where $1/\mu=1/M-1/M'$. The first sum in C is over all the N sites of the lattice and the second sum is over the impurity sites only. In D, the $\Delta\Phi_{\alpha\beta}(\mathbf{r}_i,\mathbf{r}_j)$ is the change in the harmonic force constant between an impurity site r_i and a neighboring host site r_j. We have neglected the impurity-impurity interaction because the impurity concentration is assumed to be small.

In the anharmonic part H_a, Eq. (14), we confine ourselves to V_3 and V_4 as the higher-order terms are negligible. The V_3 and V_4 have the form[13]

$$V_3(k_1,k_2,k_3)=\frac{\hbar^{1/2}\phi(k_1,k_2,k_3)}{2^{3/2}(6)N^{1/2}}(\omega_{k_1}\omega_{k_2}\omega_{k_3})^{-1/2}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\ , \tag{20}$$

$$V_4(k_1,k_2,k_3,k_4)=\frac{\hbar^{1/2}\phi(k_1,k_2,k_3,k_4)}{2^{2}(24)N}(\omega_{k_1}\omega_{k_2}\omega_{k_3}\omega_{k_4})^{-1/2}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\ , \tag{21}$$

with

$$\phi(k_1,k_2,k_3)=\sum_{i,j,m}\sum_{\alpha,\beta,\gamma}\Phi_{\alpha\beta\gamma}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_m)\epsilon_{k_1}^{\alpha}\epsilon_{k_2}^{\beta}\epsilon_{k_3}^{\gamma}e^{i(\mathbf{k}_1\cdot\mathbf{r}_i+\mathbf{k}_2\cdot\mathbf{r}_j+\mathbf{k}_3\cdot\mathbf{r}_m)}\ , \tag{22}$$

and

$$\phi(k_1,k_2,k_3,k_4)=\sum_{i,j,m,n}\sum_{\alpha,\beta,\gamma,\delta}\Phi_{\alpha\beta\gamma\delta}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_m,\mathbf{r}_n)\epsilon_{k_1}^{\alpha}\epsilon_{k_2}^{\beta}\epsilon_{k_3}^{\gamma}\epsilon_{k_4}^{\delta}e^{i(\mathbf{k}_1\cdot\mathbf{r}_i+\mathbf{k}_2\cdot\mathbf{r}_j+\mathbf{k}_3\cdot\mathbf{r}_m+\mathbf{k}_4\cdot\mathbf{r}_n)}\ . \tag{23}$$

The $\Phi_{\alpha\beta\gamma}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_m)$ and $\Phi_{\alpha\beta\gamma\delta}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_m,\mathbf{r}_n)$ are the third-order and fourth-order force constants and $\Delta(\mathbf{k})=1$ if $\mathbf{k}=\mathbf{0}$ or a reciprocal-lattice vector, and zero otherwise. We regard H_d and H_a as small perturbations of the same order.

III. EQUATIONS OF MOTION OF TWO-OPERATOR GREEN FUNCTIONS

We require the equations of motion of the two-operator retarded Green functions $\langle\langle A_k(t);A_{k'}^{\dagger}(t')\rangle\rangle$, $\langle\langle A_k(t);B_{k'}^{\dagger}(t')\rangle\rangle$, $\langle\langle B_k(t);A_{k'}^{\dagger}(t')\rangle\rangle$, and $\langle\langle B_k(t);B_{k'}^{\dagger}(t')\rangle\rangle$. From (15), we have

$$\begin{aligned}&A_k^{\dagger}=A_{-k},\quad B_k^{\dagger}=-B_{-k}\ ,\\&a_k=\tfrac{1}{2}(A_k+B_k),\quad a_k^{\dagger}=\tfrac{1}{2}(A_k^{\dagger}+B_k^{\dagger})\ .\end{aligned} \tag{24}$$

From (12) and (15) we obtain

$$[A_k,H_0]=\hbar\omega_kB_k,\quad [B_k,H_0]=\hbar\omega_kA_k\ . \tag{25}$$

We differentiate the Green functions with respect to t and t', and take the Fourier transforms to obtain

$$\begin{bmatrix}\langle\langle A_k;A_{k'}^{\dagger}\rangle\rangle_\omega\\ \langle\langle A_k;B_{k'}^{\dagger}\rangle\rangle_\omega\\ \langle\langle B_kA_{k'}^{\dagger}\rangle\rangle_\omega\\ \langle\langle B_k;B_{k'}^{\dagger}\rangle\rangle_\omega\end{bmatrix}=\frac{\delta_{kk'}}{\pi\hbar(\omega^2-\omega_k^2)}\begin{bmatrix}\omega_k\\ \omega\\ \omega\\ \omega_k\end{bmatrix}+\frac{1}{\pi^2\hbar^2(\omega^2-\omega_k^2)(\omega^2-\omega_{k'}^2)}\begin{bmatrix}\omega^2&\omega\omega_{k'}&\omega_k\omega&\omega_k\omega_{k'}\\ \omega\omega_{k'}&\omega^2&\omega_k\omega_{k'}&\omega_k\omega\\ \omega_k\omega&\omega_k\omega_{k'}&\omega^2&\omega\omega_{k'}\\ \omega_k\omega_{k'}&\omega_k\omega&\omega\omega_{k'}&\omega^2\end{bmatrix}\begin{bmatrix}P_{11kk'}\\ P_{12kk'}\\ P_{21kk'}\\ P_{22kk'}\end{bmatrix}\ . \tag{26}$$

In the zeroth-order approximation we take only the first term in (26) and obtain

$$\begin{aligned}&\langle\langle A_k;A_{k'}^{\dagger}\rangle\rangle_\omega^{(0)}=\frac{\omega_k\delta_{kk'}}{\pi\hbar(\omega^2-\omega_k^2)}=\langle\langle B_k;B_{k'}^{\dagger}\rangle\rangle_\omega^{(0)}\ ,\\&\langle\langle A_k;B_{k'}^{\dagger}\rangle\rangle_\omega^{(0)}=\frac{\omega\delta_{kk'}}{\pi\hbar(\omega^2-\omega_k^2)}=\langle\langle B_k;A_{k'}^{\dagger}\rangle\rangle_\omega^{(0)}\ .\end{aligned} \tag{27}$$

Thus, in the zeroth-order approximation

$$\langle A_{k_1}A_{k_2}\rangle^{(0)}=\delta_{-k_1k_2}n_{k_1}\ , \tag{28}$$

where

$$n_k=\coth(\tfrac{1}{2}\beta\hbar\omega_k)\ ,\ \beta=1/k_BT\ . \tag{29}$$

The polarization vectors are of the form

$$
\begin{aligned}
P_{11kk'} &= \frac{\pi}{2}\langle[[A_k,H_1],A_{k'}^\dagger]\rangle - \pi^2\langle\langle[A_k,H_1];[A_{k'}^\dagger,H_1]\rangle\rangle \\
&= P_{11kk'}^{(1)} + P_{11kk'}^{(2)}(\omega) + \cdots , \\
P_{12kk'} &= \frac{\pi}{2}\langle[[A_k,H_1],B_{k'}^\dagger]\rangle - \pi^2\langle\langle[A_k,H_1];[B_{k'}^\dagger,H_1]\rangle\rangle \\
&= P_{12kk'}^{(1)} + P_{12kk'}^{(2)}(\omega) + \cdots , \\
P_{21kk'} &= \frac{\pi}{2}\langle[[B_k,H_1],A_{k'}^\dagger]\rangle - \pi^2\langle\langle[B_k,H_1];[A_{k'}^\dagger,H_1]\rangle\rangle \\
&= P_{21kk'}^{(1)} + P_{21kk'}^{(2)}(\omega) + \cdots , \\
P_{22kk'} &= \frac{\pi}{2}\langle[[B_k,H_1],B_{k'}^\dagger]\rangle - \pi^2\langle\langle[B_k,H_1];[B_{k'}^\dagger,H_1]\rangle\rangle \\
&= P_{22kk'}^{(1)} + P_{22kk'}^{(2)} + \cdots ,
\end{aligned}
\tag{30}
$$

where the first terms are of first order and independent of ω, and the second terms give the higher-order contributions and are functions of ω. Using (11)–(14), the first-order polarization operators are

$$
\begin{aligned}
P_{11kk'}^{(1)} &= \frac{\pi}{2}\langle[[A_k,H_1],A_{k'}^\dagger]\rangle = 4\pi\hbar C(-k,k') , \\
P_{12kk'}^{(1)} &= \frac{\pi}{2}\langle[[A_k,H_1],B_{k'}^\dagger]\rangle = 0 , \\
P_{21kk'}^{(1)} &= \frac{\pi}{2}\langle[[B_k,H_1],A_{k'}^\dagger]\rangle = 0 , \\
P_{22kk'}^{(1)} &= \frac{\pi}{2}\langle[[B_k,H_1],B_{k'}^\dagger]\rangle \\
&= 4\pi\hbar D(-k,k') + 24\pi\hbar \sum_{k_1,k_2} V_4(-k,k',k_1,k_2)\langle A_{k_1}A_{k_2}\rangle \\
&\equiv 4\pi\hbar\bar{D}(-k,k') .
\end{aligned}
\tag{31}
$$

Using the higher-order Green function we obtain the second-order polarization operators,

$$
\begin{aligned}
P_{11kk'}^{(2)}(\omega) &= 16\pi^2\hbar^2 \sum_{k_1} C(-k,k_1)C(k',-k_1)\frac{\omega_{k_1}}{\pi\hbar(\omega^2-\omega_{k_1}^2)} , \\
P_{12kk'}^{(2)}(\omega) &= 16\pi^2\hbar^2 \sum_{k_1} C(-k,k_1)\bar{D}(k',-k_1)\frac{\omega}{\pi\hbar(\omega^2-\omega_{k_1}^2)} , \\
P_{21kk'}^{(2)}(\omega) &= 16\pi^2\hbar^2 \sum_{k_1} \bar{D}(-k,k_1)C(k',-k_1)\frac{\omega}{\pi\hbar(\omega^2-\omega_{k_1}^2)} , \\
P_{22kk'}^{(2)}(\omega) &= 16\pi^2\hbar^2 \sum_{k_1} \bar{D}(-k,k_1)\bar{D}(k',-k_1)\frac{\omega_{k_1}}{\pi\hbar(\omega^2-\omega_{k_1}^2)} \\
&\quad + 36\pi^2\hbar^2 \sum_{k_1,k_2} V_3(-k,k_1,k_2)V_3(k',-k_1,-k_2)\left[\frac{(n_{k_1}+n_{k_2})(\omega_{k_1}+\omega_{k_2})}{\pi\hbar[\omega^2-(\omega_{k_1}+\omega_{k_2})^2]} + \frac{(n_{k_1}-n_{k_2})(\omega_{k_1}-\omega_{k_2})}{\pi\hbar[\omega^2-(\omega_{k_1}-\omega_{k_2})^2]}\right] \\
&\quad + 96\pi^2\hbar^2 \sum_{k_1,k_2,k_3}{}' V_4(-k,k_1,k_2,k_3)V_4(k,-k_1,-k_2,-k_3)
\end{aligned}
\tag{32}
$$

$$\times\left[(1+n_{k_1}n_{k_2}+n_{k_2}n_{k_3}+n_{k_3}n_{k_1})\frac{\omega_{k_1}+\omega_{k_2}+\omega_{k_3}}{\pi\hbar[\omega^2-(\omega_{k_1}+\omega_{k_2}+\omega_{k_3})^2]}\right.$$
$$\left.+(\omega_{k_1}\to-\omega_{k_1})+(\omega_{k_2}\to-\omega_{k_2})+(\omega_{k_3}\to-\omega_{k_3})\right],$$

where $\sum'$ means that terms with equal and opposite wave vectors are excluded.

Substituting (31) and (32) into (26), we obtain the Green functions up to second order. For $k\neq k'$ the zeroth-order term vanishes. For the case $k=k'$, we can incorporate the first-order term in the zeroth-order term by a renormalization of the frequency by writing

$$\begin{aligned}&\omega_k^{(1)}=\omega_k+4\hbar C(-k,k),\quad \omega_k^{(2)}=\omega_k+4\hbar\bar{D}(-k,k)\,,\\&\tilde{\omega}_k^2=\omega_k^{(1)}\omega_k^{(2)},\quad \tilde{n}_k=\coth(\tfrac{1}{2}\beta\hbar\tilde{\omega}_k)\,,\\&\bar{\omega}_k^{(1)}=\omega_k+S_1,\quad \bar{\omega}_k^{(2)}=\omega_k+S_2+S_V,\quad \tilde{\bar{\omega}}_k^2=\bar{\omega}_k^{(1)}\bar{\omega}_k^{(2)}\,,\end{aligned}\tag{33}$$

where

$$\begin{aligned}S_1&=4\hbar C(-k,k)+16\hbar\sum_{k_1\,(\neq k)}\frac{C(-k,k_1)}{\omega_k^2-\omega_{k_1}^2}[C(k,-k_1)\omega_{k_1}+\bar{D}(k,-k_1)\omega_k]\,,\\S_2&=4\hbar\bar{D}(-k,k)+16\hbar\sum_{k_1\,(\neq k)}\frac{\bar{D}(-k,k_1)}{\omega_k^2-\omega_{k_1}^2}[C(k,-k_1)\omega_k+\bar{D}(k,-k_1)\omega_{k_1}]\,,\\S_V&=36\hbar\sum_{k_1,k_2}V_3(-k,k_1,k_2)V_3(k,-k_1,-k_2)\left[\frac{(\tilde{n}_{k_1}+\tilde{n}_{k_2})(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2})}{\tilde{\omega}_k^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2})^2}+\frac{(\tilde{n}_{k_1}-\tilde{n}_{k_2})(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2})}{\tilde{\omega}_k^2-(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2})^2}\right]\\&\quad+96\hbar\sum_{k_1,k_2,k_3}{}'\,V_4(-k,k_1,k_2,k_3)V_4(k,-k_1,-k_2,-k_3)\\&\quad\times\left[(1+\tilde{n}_{k_1}\tilde{n}_{k_2}+\tilde{n}_{k_2}\tilde{n}_{k_3}+\tilde{n}_{k_3}\tilde{n}_{k_1})\frac{\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3}}{\tilde{\omega}_k^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3})^2}\right.\\&\quad\left.+(\tilde{\omega}_{k_1}\to-\tilde{\omega}_{k_1})+(\tilde{\omega}_{k_2}\to-\tilde{\omega}_{k_2})+(\tilde{\omega}_{k_3}\to-\tilde{\omega}_{k_3})\right].\end{aligned}\tag{34}$$

For $k=k'$, we can now write (26) as

$$\begin{bmatrix}\langle\langle A_k;A_k^\dagger\rangle\rangle_\omega\\\langle\langle A_k;B_k^\dagger\rangle\rangle_\omega\\\langle\langle B_k;A_k^\dagger\rangle\rangle_\omega\\\langle\langle B_k;B_k^\dagger\rangle\rangle_\omega\end{bmatrix}=\frac{1}{\pi\hbar(\omega^2-\tilde{\bar{\omega}}_k^2)}\begin{bmatrix}\bar{\omega}_k^{(1)}\\\omega\\\omega\\\bar{\omega}_k^{(2)}\end{bmatrix}+\cdots\,,\tag{35}$$

where the ellipsis represents unspecified second- and higher-order terms.

IV. THERMAL CONDUCTIVITY

The total heat-flux operator given by Hardy[14] leads to the thermal conductivity[8] expression

$$\begin{aligned}&K=K_d+K_{\rm nd}+K_c+K_{\rm anh}+K_{\rm imp}\,,\\&K_c=K_c^{(1)}+K_c^{(2)}+K_c^{(3)},\quad K_{\rm anh}=K_1+K_2\,,\end{aligned}\tag{36}$$

where the various contributions are defined in Eqs. (4)—(23) of Ref. 8. The K_d is the diagonal contribution and $K_{\rm nd}$ is the nondiagonal contribution due to the nondiagonal term in the energy-flux operator. The K_c represents the contribution to the thermal conductivity arising from terms that are cubic functions of position and momentum operators in the harmonic approximation of the energy-flux operator. Finally, $K_{\rm anh}$ and $K_{\rm imp}$ are contributions from the perturbation term in the energy flux due to cubic anharmonic forces and lattice imperfection, respectively.

From (31), (35), and (36), we obtain

$$K_d=\frac{\pi\hbar^2 k_B\beta^2}{3V}\left[\sum_{\mathbf{k},s}\left\{\omega_{\mathbf{k}s}^2\mathbf{v}_{\mathbf{k}s}^2\frac{e^{\beta\hbar\tilde{\tilde{\omega}}_{\mathbf{k}s}}}{(e^{\beta\hbar\tilde{\tilde{\omega}}_{\mathbf{k}s}}-1)^2}\right.\right.$$
$$\left.-2\mathbf{v}_{\mathbf{k}s}^2[C(-\mathbf{k},s;-\mathbf{k}s)-\bar{D}(-\mathbf{k},s;-\mathbf{k},s)][C(\mathbf{k},s;\mathbf{k},s)-\bar{D}(\mathbf{k},s;\mathbf{k},s)]\frac{e^{\beta\hbar\omega_{\mathbf{k}s}}}{(e^{\beta\hbar\omega_{\mathbf{k}s}}-1)^2}\right\}$$
$$-2\sum_{\substack{\mathbf{k},s,s'\\ \omega_{\mathbf{k}s}=\omega_{\mathbf{k}s'}}}\mathbf{v}_{\mathbf{k}s}\cdot\mathbf{v}_{\mathbf{k}s'}\{[C(-\mathbf{k},s',\mathbf{k},s')-\bar{D}(-\mathbf{k},s;\mathbf{k},s')][C(-\mathbf{k},s';\mathbf{k},s)-\bar{D}(-\mathbf{k},s';\mathbf{k},s)]$$
$$-[C(-\mathbf{k},s;-\mathbf{k},s')-\bar{D}(-\mathbf{k},s;-\mathbf{k},s')][C(\mathbf{k},s';\mathbf{k},s)-\bar{D}(\mathbf{k},s';\mathbf{k},s)]\}\frac{e^{\beta\hbar\omega_{\mathbf{k}s}}}{(e^{\beta\hbar\omega_{\mathbf{k}s}}-1)^2}$$
$$+8\sum_{\mathbf{k},s}\sum_{\mathbf{k}',s'}\omega_{\mathbf{k}s}\omega_{\mathbf{k}'s'}\mathbf{v}_{\mathbf{k}s}\cdot\mathbf{v}_{\mathbf{k}'s'}\left\{[P_a(-\mathbf{k},s;\mathbf{k}',s')P_b(\mathbf{k},s;-\mathbf{k}',s')\right.$$
$$-P_b(-\mathbf{k},s;-\mathbf{k}',s')P_a(\mathbf{k},s;\mathbf{k}',s')]\frac{e^{\beta\hbar\omega_{\mathbf{k}s}}}{(e^{\beta\hbar\omega_{\mathbf{k}s}}-1)^2}$$
$$+[P_b(-\mathbf{k},s;\mathbf{k}',s')P_a(\mathbf{k},s;-\mathbf{k}',s')$$
$$\left.\left.-P_b(-\mathbf{k},s;\mathbf{k}',s')P_a(\mathbf{k},s;\mathbf{k}',s')]\frac{e^{\beta\hbar\omega_{\mathbf{k}'s'}}}{(e^{\beta\hbar\omega_{\mathbf{k}'s'}}-1)^2}\right\}\right],\qquad(37)$$

$$K_{\rm nd}=\frac{\pi\hbar^2k_B\beta^2}{6V}\sum_{\mathbf{k},s,s'}\sum_{\mathbf{k}_1,s_1,s_1'}\omega_{\mathbf{k}s}\omega_{\mathbf{k}_1s_1}\mathbf{v}_{\mathbf{k}ss'}\cdot\mathbf{v}_{\mathbf{k}_1s_1s_1'}$$
$$\times\left\{[P_a(-\mathbf{k},s;\mathbf{k}_1,s_1)P_b(\mathbf{k},s';-\mathbf{k}_1,s_1')-P_b(-\mathbf{k},s;-\mathbf{k}_1,s_1)P_a(\mathbf{k},s';\mathbf{k}_1,s_1')]\frac{e^{\beta\hbar\omega_{\mathbf{k}s}}}{(e^{\beta\hbar\omega_{\mathbf{k}s}}-1)^2}\right.$$
$$\left.+[P_b(-\mathbf{k},s;\mathbf{k}_1,s_1)P_a(\mathbf{k},s';-\mathbf{k}_1,s_1')-P_b(-\mathbf{k},s;-\mathbf{k}_1,s_1)P_a(\mathbf{k},s';\mathbf{k}_1,s_1')]\frac{e^{\beta\hbar\omega_{\mathbf{k}_1s_1}}}{(e^{\beta\hbar\omega_{\mathbf{k}_1s_1}}-1)^2}\right\},\qquad(38)$$

$$K_c^{(1)}=\frac{3\hbar^2k_B\beta^2}{V}$$
$$\times\sum_{\mathbf{k},s,\mathbf{k}',s',\mathbf{k}'',s''}\ \sum_{\mathbf{k}_1,s_1,\mathbf{k}_1',s_1',\mathbf{k}_1''s_1''}\mathbf{X}_{\mathbf{k}s\mathbf{k}'s'\mathbf{k}''s''}\cdot\mathbf{X}^*_{\mathbf{k}_1s_1\mathbf{k}_1's_1'\mathbf{k}_1''s_1''}\delta^{(2)}V_3(-\mathbf{k},s;\mathbf{k}',s';\mathbf{k}'',s'')$$
$$\times V_3(\mathbf{k}_1,s_1;-\mathbf{k}_1',s_1';-\mathbf{k}_1'',s_1'')\tilde{\omega}_{\mathbf{k}s}\tilde{\omega}_{\mathbf{k}_1s_1}\left\{\frac{\omega^{(1)}_{\mathbf{k}'s'}\omega^{(1)}_{\mathbf{k}''s''}}{\tilde{\omega}_{\mathbf{k}'s'}\tilde{\omega}_{\mathbf{k}''s''}}\right\}$$
$$\times\left\{\frac{(\tilde{n}_{\mathbf{k}',s'}+\tilde{n}_{\mathbf{k}''s''})^2}{[\tilde{\omega}^2_{\mathbf{k}s}-(\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})^2][\tilde{\omega}^2_{\mathbf{k}_1s_1}-(\tilde{\omega}_{\mathbf{k}_1's_1'}+\tilde{\omega}_{\mathbf{k}_1''s_1''})^2]}\frac{e^{\beta\hbar(\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})}}{(e^{\beta\hbar(\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})}-1)^2}\right.$$
$$\left.+\frac{(\tilde{n}_{\mathbf{k}'s'}-\tilde{n}_{\mathbf{k}''s''})^2}{[\tilde{\omega}^2_{\mathbf{k}s}-(\tilde{\omega}_{\mathbf{k}'s'}-\tilde{\omega}_{\mathbf{k}''s''})^2][\tilde{\omega}^2_{\mathbf{k}_1s_1}-(\tilde{\omega}_{\mathbf{k}_1's_1'}-\tilde{\omega}_{\mathbf{k}_1''s_1''})^2]}\frac{e^{\beta\hbar(\tilde{\omega}_{\mathbf{k}'s'}-\tilde{\omega}_{\mathbf{k}''s''})}}{(e^{\beta\hbar(\tilde{\omega}_{\mathbf{k}'s'}-\tilde{\omega}_{\mathbf{k}''s''})}-1)^2}\right\},\qquad(39)$$

$$K_c^{(2)}=\frac{3\hbar^2 k_B\beta^2}{V}\times\sum_{\mathbf{k},s,\mathbf{k}',s',\mathbf{k}'',s''}\;\sum_{\mathbf{k}_1,s_1,\mathbf{k}_1',s_1',\mathbf{k}_1'',s_1''}\mathbf{Y}_{\mathbf{k}s\mathbf{k}'s'\mathbf{k}''s''}\cdot\mathbf{Y}^*_{\mathbf{k}_1s_1\mathbf{k}_1's_1'\mathbf{k}_1''s_1''}$$
$$\times\delta^{(2)}V_3(-\mathbf{k},s,\mathbf{k}',s';\mathbf{k}'',s'')V_3(\mathbf{k}_1,s_1;-\mathbf{k},s';-\mathbf{k}'',s'')\tilde{\omega}_{\mathbf{k}s}\tilde{\omega}_{\mathbf{k}_1s_1}\left[\frac{\omega^{(2)}_{\mathbf{k}'s'}\omega^{(2)}_{\mathbf{k}''s''}}{\tilde{\omega}_{\mathbf{k}'s'}\tilde{\omega}_{\mathbf{k}''s''}}\right]$$
$$\times\left[\frac{(\tilde{n}_{\mathbf{k}'s'}+\tilde{n}_{\mathbf{k}''s''})^2}{[\tilde{\omega}^2_{\mathbf{k}s}-(\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})^2][\tilde{\omega}_{\mathbf{k}_1s_1}-(\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})^2]}\frac{e^{\beta\hbar(\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})}}{(e^{\beta\hbar(\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})}-1)^2}\right.$$
$$\left.+\frac{(\tilde{n}_{\mathbf{k}'s'}-\tilde{n}_{\mathbf{k}''s''})^2}{[\tilde{\omega}^2_{\mathbf{k}s}-(\tilde{\omega}_{\mathbf{k}'s'}-\tilde{\omega}_{\mathbf{k}''s''})^2][\tilde{\omega}^2_{\mathbf{k}_1s_1}-(\tilde{\omega}_{\mathbf{k}'s'}-\tilde{\omega}_{\mathbf{k}''s''})^2]}\frac{e^{\beta\hbar(\tilde{\omega}_{\mathbf{k}'s'}-\tilde{\omega}_{\mathbf{k}''s''})}}{(e^{\beta\hbar(\tilde{\omega}_{\mathbf{k}'s'}-\tilde{\omega}_{\mathbf{k}''s''})}-1)^2}\right], \tag{40}$$

$$K_c^{(3)}=\frac{3\hbar^2 k_B\beta^2}{V}\times\sum_{\mathbf{k},s,\mathbf{k}',s',\mathbf{k}'',s''}\;\sum_{\mathbf{k}_1,s_1,\mathbf{k}_1',s_1',\mathbf{k}_1'',s_1''}\mathbf{Z}_{\mathbf{k}s\mathbf{k}'s'\mathbf{k}''s''}\cdot\mathbf{Z}^*_{\mathbf{k}_1s_1\mathbf{k}_1's_1'\mathbf{k}_1''s_1''}\delta^{(2)}V_3(-\mathbf{k}'',s'';\mathbf{k},s;\mathbf{k}',s')$$
$$\times V_3(\mathbf{k}_1'',s_1'';-\mathbf{k},s;-\mathbf{k}',s')\tilde{\omega}_{\mathbf{k}''s''}\tilde{\omega}_{\mathbf{k}_1''s_1''}\left[\frac{\omega^{(2)}_{\mathbf{k}s}\omega^{(2)}_{\mathbf{k}'s'}}{\tilde{\omega}_{\mathbf{k}s}\tilde{\omega}_{\mathbf{k}'s'}}\right]$$
$$\times\left[\frac{(\tilde{n}_{\mathbf{k}s}+\tilde{n}_{\mathbf{k}'s'})^2}{[\tilde{\omega}^2_{\mathbf{k}''s''}-(\tilde{\omega}_{\mathbf{k}s}+\tilde{\omega}_{\mathbf{k}'s'})^2][\tilde{\omega}_{\mathbf{k}_1''s_1''}-(\tilde{\omega}_{\mathbf{k}s}+\tilde{\omega}_{\mathbf{k}'s'})^2]}\frac{e^{\beta\hbar(\tilde{\omega}_{\mathbf{k}s}+\tilde{\omega}_{\mathbf{k}'s'})}}{(e^{\beta\hbar(\tilde{\omega}_{\mathbf{k}s}+\tilde{\omega}_{\mathbf{k}'s'})}-1)^2}\right.$$
$$\left.+\frac{(\tilde{n}_{\mathbf{k}s}-\tilde{n}_{\mathbf{k}'s'})^2}{[\tilde{\omega}^2_{\mathbf{k}''s''}-(\tilde{\omega}_{\mathbf{k}s}-\tilde{\omega}_{\mathbf{k}'s'})^2][\tilde{\omega}_{\mathbf{k}_1''s_1''}-(\tilde{\omega}_{\mathbf{k}s}-\tilde{\omega}_{\mathbf{k}'s'})^2]}\frac{e^{\beta\hbar(\tilde{\omega}_{\mathbf{k}s}-\tilde{\omega}_{\mathbf{k}'s'})}}{(e^{\beta\hbar(\tilde{\omega}_{\mathbf{k}s}-\tilde{\omega}_{\mathbf{k}'s'})}-1)^2}\right], \tag{41}$$

$$K_1=\frac{3\hbar^2 k_B\beta^2}{V}\times\sum_{\mathbf{k},s,\mathbf{k}',s',\mathbf{k}'',s''}\;\sum_{\mathbf{k}_1,s_1,\mathbf{k}_1',s_1',\mathbf{k}_1'',s_1''}\mathbf{J}_{\mathbf{k}s\mathbf{k}'s'\mathbf{k}''s''}\cdot\mathbf{J}^*_{\mathbf{k}_1s_1\mathbf{k}_1's_1'\mathbf{k}_1''s_1''}\delta^{(2)}V_3(-\mathbf{k},s;\mathbf{k}',s';\mathbf{k}'',s'')$$
$$\times V_3(\mathbf{k}_1,s_1;-\mathbf{k}',s';-\mathbf{k}'',s'')\tilde{\omega}_{\mathbf{k}s}\tilde{\omega}_{\mathbf{k}_1s_1}\left[\frac{\omega^{(2)}_{\mathbf{k}'s'}\omega^{(2)}_{\mathbf{k}''s''}}{\tilde{\omega}_{\mathbf{k}'s'}\tilde{\omega}_{\mathbf{k}''s''}}\right]$$
$$\times\left[\frac{(\tilde{n}_{\mathbf{k}'s'}+\tilde{n}_{\mathbf{k}''s''})^2}{[\tilde{\omega}^2_{\mathbf{k}s}-(\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})^2][\tilde{\omega}_{\mathbf{k}_1s_1}-(\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})^2]}\frac{e^{\beta\hbar(\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})}}{(e^{\beta\hbar(\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})}-1)^2}\right.$$
$$\left.+\frac{(\tilde{n}_{\mathbf{k}'s'}-\tilde{n}_{\mathbf{k}''s''})^2}{[\tilde{\omega}^2_{\mathbf{k}s}-(\tilde{\omega}_{\mathbf{k}'s'}-\tilde{\omega}_{\mathbf{k}''s''})^2][\tilde{\omega}^2_{\mathbf{k}_1s_1}-(\tilde{\omega}_{\mathbf{k}'s'}-\tilde{\omega}_{\mathbf{k}''s''})^2]}\frac{e^{\beta\hbar(\tilde{\omega}_{\mathbf{k}'s'}-\tilde{\omega}_{\mathbf{k}''s''})}}{(e^{\beta\hbar(\tilde{\omega}_{\mathbf{k}'s'}-\tilde{\omega}_{\mathbf{k}''s''})}-1)^2}\right], \tag{42}$$

$$K_2=\frac{4\hbar^2k_B\beta^2}{V}\sum_{\mathbf{k},s,\mathbf{k}',s',\mathbf{k}'',s'',\mathbf{k}''',s'''}\sum_{\mathbf{k}_1s_1,\mathbf{k}_1's_1',\mathbf{k}_1''s_1'',\mathbf{k}_1'''s_1'''}\mathbf{J}_{\mathbf{k}s\mathbf{k}'s'\mathbf{k}''s''\mathbf{k}'''s'''}\cdot\mathbf{J}^*_{\mathbf{k}_1s_1\mathbf{k}_1's_1'\mathbf{k}_1''s_1''\mathbf{k}_1'''s_1'''}$$
$$\times\delta^{(3)}V_4(-\mathbf{k}''',s''';\mathbf{k},s;\mathbf{k}',s';\mathbf{k}'',s'')V_4(\mathbf{k}_1''',s_1''';-\mathbf{k},s;-\mathbf{k}',s';-\mathbf{k}'',s'')$$
$$\times\tilde{\omega}_{\mathbf{k}'''s'''}\tilde{\omega}_{\mathbf{k}_1'''s_1'''}\left[\frac{\omega^{(2)}_{\mathbf{k}s}\omega^{(2)}_{\mathbf{k}'s'}\omega^{(2)}_{\mathbf{k}''s''}}{\tilde{\omega}_{\mathbf{k}s}\tilde{\omega}_{\mathbf{k}'s'}\tilde{\omega}_{\mathbf{k}''s''}}\right]$$
$$\times\left\{\frac{(1+\tilde{n}_{\mathbf{k}s}\tilde{n}_{\mathbf{k}'s'}+\tilde{n}_{\mathbf{k}'s'}\tilde{n}_{\mathbf{k}''s''}+\tilde{n}_{\mathbf{k}''s''}\tilde{n}_{\mathbf{k}s})(\tilde{\omega}_{\mathbf{k}s}+\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})}{[\tilde{\omega}^2_{\mathbf{k}'''s'''}-(\tilde{\omega}_{\mathbf{k}s}+\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})^2][\tilde{\omega}^2_{\mathbf{k}_1'''s_1'''}-(\tilde{\omega}_{\mathbf{k}s}+\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})^2]}\right.$$
$$\times\frac{e^{\beta\hbar(\tilde{\omega}_{\mathbf{k}s}+\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})}}{(e^{\beta\hbar(\tilde{\omega}_{\mathbf{k}s}+\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})}-1)^2}$$
$$\left.+(\tilde{\omega}_{\mathbf{k}s}\to-\tilde{\omega}_{\mathbf{k}s})+(\tilde{\omega}_{\mathbf{k}'s'}\to-\tilde{\omega}_{\mathbf{k}'s'})+(\tilde{\omega}_{\mathbf{k}''s''}\to-\tilde{\omega}_{\mathbf{k}''s''})\right\},\tag{43}$$

$$K_{\text{imp}}=\frac{\pi\hbar^2k_B\beta^2}{6V}\sum_{\mathbf{k},s,\mathbf{k}',s'}\sum_{\mathbf{k}_1,s_1,\mathbf{k}_1',s_1'}\mathbf{J}_{\mathbf{k}s\mathbf{k}'s'}\cdot\mathbf{J}^*_{\mathbf{k}_1s_1\mathbf{k}_1's_1'}$$
$$\times\left\{-4[C(-\mathbf{k},s;\mathbf{k}_1,s_1)-\bar{D}(-\mathbf{k},s;\mathbf{k}_1,s_1)][C(-\mathbf{k}',s';\mathbf{k}_1's_1')-\bar{D}(-\mathbf{k}',s';\mathbf{k}_1',s_1')]\right.$$
$$\times\frac{e^{\beta\hbar\omega_{\mathbf{k}s}}}{(e^{\beta\hbar\omega_{\mathbf{k}s}}-1)^2}(\omega_{\mathbf{k}s}=\omega_{\mathbf{k}'s'}=\omega_{\mathbf{k}_1s_1}=\omega_{\mathbf{k}_1's_1'})+[P_a(-\mathbf{k},s;\mathbf{k}_1,s_1)P_b(-k',s';\mathbf{k}_1',s_1')$$
$$-P_b(-\mathbf{k},s;\mathbf{k}_1',s_1')P_a(-\mathbf{k}',s';\mathbf{k}_1,s_1)]$$
$$\times\delta_{\omega_{\mathbf{k}s}\omega_{\mathbf{k}'s'}}\frac{e^{\beta\hbar\omega_{\mathbf{k}s}}}{(e^{\beta\hbar\omega_{\mathbf{k}s}}-1)^2}+[P_b(-\mathbf{k},s;\mathbf{k}_1',s_1')P_a(-\mathbf{k}',s';\mathbf{k}_1,s_1)\delta_{\omega_{\mathbf{k}s}\omega_{\mathbf{k}_1s_1}}$$
$$-P_b(-\mathbf{k},s;\mathbf{k}_1,s_1)P_a(-\mathbf{k}',s';\mathbf{k}_1',s_1')\delta_{\omega_{\mathbf{k}s}\omega_{\mathbf{k}_1's_1'}}]$$
$$\times\frac{e^{\beta\hbar\omega_{\mathbf{k}s}}}{(e^{\beta\hbar\omega_{\mathbf{k}s}}-1)^2}+[P_b(-\mathbf{k},s;\mathbf{k}_1,s_1)P_a(-\mathbf{k}',s';\mathbf{k}_1',s_1')$$
$$-P_b(-\mathbf{k},s;\mathbf{k}_1',s_1')P_a(-\mathbf{k}',s';\mathbf{k}_1,s_1)]$$
$$\times\delta_{\omega_{\mathbf{k}_1s_1}\omega_{\mathbf{k}_1's_1'}}\frac{e^{\beta\hbar\omega_{\mathbf{k}_1s_1}}}{(e^{\beta\hbar\omega_{\mathbf{k}_1s_1}}-1)^2}+[P_b(-\mathbf{k},s;\mathbf{k}_1',s_1')P_a(-\mathbf{k}',s';\mathbf{k}_1,s_1)\delta_{\omega_{\mathbf{k}'s'}\omega_{\mathbf{k}_1's_1'}}$$
$$-P_b(-\mathbf{k},s;\mathbf{k}_1,s_1)P_a(-\mathbf{k}',s';\mathbf{k}_1',s_1')\delta_{\omega_{\mathbf{k}'s'}\omega_{\mathbf{k}_1s_1}}]$$
$$\left.\times\frac{e^{\beta\hbar\omega_{\mathbf{k}'s'}}}{(e^{\beta\hbar\omega_{\mathbf{k}'s'}}-1)^2}\right\},\tag{44}$$

where

$$\delta^{(2)}=\delta_{k_1k_1'}\delta_{k_2k_2'}+\delta_{k_1k_2'}\delta_{k_2k_1'},$$
$$\delta^{(3)}=\delta_{123}+\delta_{213}+\delta_{321},\quad\delta_{123}=\delta_{k_1k_1'}(\delta_{k_2k_2'}\delta_{k_3k_3'}+\delta_{k_2k_3'}\delta_{k_3k_2'}),$$
$$P_a(\mathbf{k},s;\mathbf{k}',s')=\frac{4[C(\mathbf{k},s;\mathbf{k}',s')\omega_{\mathbf{k}s}+\bar{D}(\mathbf{k},s;\mathbf{k}',s')\omega_{\mathbf{k}'s'}]}{(\omega^2_{\mathbf{k}s}-\omega^2_{\mathbf{k}'s'})},$$
$$P_b(\mathbf{k},s;\mathbf{k}',s')=\frac{4[C(\mathbf{k},s;\mathbf{k}',s')\omega_{\mathbf{k}'s'}+\bar{D}(\mathbf{k},s;\mathbf{k}',s')\omega_{\mathbf{k}s}]}{(\omega^2_{\mathbf{k}s}-\omega^2_{\mathbf{k}'s'})}.\tag{45}$$

The first term in K_d is of zeroth order, while all other terms are of second order. Even the zeroth-order term depends both on the temperature and concentration and so their effect on K will show up in experiments.

V. SHEAR VISCOSITY

According to McLennan,[15] the shear viscosity has the form

$$\eta_{ijlm}=\beta V\lim_{\epsilon\to 0}\int_0^t dt\, e^{-\epsilon t}\langle J_{ij}(t)[J_{1m}(t)-\hat{J}_{1m}]\rangle \ , \tag{46}$$

where the momentum flux operator as given by de Vault[16] is

$$J_{ij}(t)=V^{-1}\sum_{\mathbf{k},s}\hbar\omega_{\mathbf{k}s}[a^\dagger_{\mathbf{k}s}(t)a_{\mathbf{k}s}(t)+\tfrac{1}{2}]\gamma^{ij}_{\mathbf{k}s} \ , \tag{47}$$

$$\hat{J}_{ij}=V^{-1}\sum_{\mathbf{k},s}\hbar\omega_{\mathbf{k}s}\gamma^{ij}_{\mathbf{k}s}(\langle a^\dagger_{\mathbf{k}s}a_{\mathbf{k}s}\rangle+\tfrac{1}{2})+V^{-1}\gamma^{ij}\sum_{\mathbf{k}s}\hbar\omega_{\mathbf{k}s}(a^\dagger_{\mathbf{k}s}a_{\mathbf{k}s}-\langle a^\dagger_{\mathbf{k}s}a_{\mathbf{k}s}\rangle) \ . \tag{48}$$

Here $\gamma^{ij}_{\mathbf{k}s}$ is the generalized Grüneisen parameter and

$$\gamma^{ij}=\frac{1}{12\pi}\int d\mathbf{k}\sum_s\gamma^{ij}_{\mathbf{k}s} \ . \tag{49}$$

For cubic symmetry we can approximate by

$$\langle J_{ij}(t)\rangle=V^{-1}\langle H_0\rangle\gamma^{ij} \ . \tag{50}$$

Then

$$\eta_{ijlm}=V^{-1}\hbar^2\beta\lim_{\epsilon\to 0}\int_0^t dt\, e^{-\epsilon t}\sum_{\mathbf{k},s}\sum_{\mathbf{k}',s'}\omega_{\mathbf{k}s}\omega_{\mathbf{k}'s'}\gamma^{ij}_{\mathbf{k}s}(\gamma^{lm}_{\mathbf{k}'s'}-\gamma^{lm})\langle a^\dagger_{\mathbf{k}s}(t)a_{\mathbf{k}s}(t)(a^\dagger_{\mathbf{k}'s'}a_{\mathbf{k}'s'}-\langle a^\dagger_{\mathbf{k}'s'}a_{\mathbf{k}'s'}\rangle)\rangle \ . \tag{51}$$

We can decouple the correlation functions omitting equal-time correlation functions, as they do not contribute to the integral, in the following way:

$$\langle a^\dagger_{\mathbf{k}s}(t)a_{\mathbf{k}'s'}(0)\rangle\langle a_{\mathbf{k}s}(t)a_{\mathbf{k}'s'}(0)\rangle+\langle a^\dagger_{\mathbf{k}s}(t)a^\dagger_{\mathbf{k}'s'}(0)\rangle\langle a_{\mathbf{k}s}(t)a_{\mathbf{k}'s'}(0)\rangle \ .$$

Using (15), (31), and (35), we finally get

$$\begin{aligned}\eta_{ijlm}=\frac{2\pi\hbar^2\beta}{V}\Bigg[&\sum_{\mathbf{k},s}\omega^2_{\mathbf{k}s}\gamma^{ij}_{\mathbf{k}s}(\gamma^{lm}_{\mathbf{k}s}-\gamma^{lm})\left[\frac{e^{\beta\hbar\tilde{\bar{\omega}}_{\mathbf{k}s}}}{(e^{\beta\hbar\tilde{\bar{\omega}}_{\mathbf{k}s}}-1)^2}+4\hbar^2\,|\,C(-\mathbf{k},s;\mathbf{k},s)-\bar{D}(-\mathbf{k},s;\mathbf{k},s)\,|^2\frac{e^{\beta\hbar\omega_{\mathbf{k}s}}}{(e^{\beta\hbar\omega_{\mathbf{k}s}}-1)^2}\right]\\
&+\sum_{\substack{\mathbf{k},s,s'\\(\omega_{\mathbf{k}s}=\omega_{\mathbf{k}'s'})}}\gamma^{ij}_{\mathbf{k}s}(\gamma^{lm}_{\mathbf{k}s'}-\gamma^{lm})2\hbar^2\,|\,C(-\mathbf{k},s;\mathbf{k},s')-\bar{D}(-\mathbf{k},s;\mathbf{k},s')\,|^2\frac{e^{\beta\hbar\omega_{\mathbf{k}s}}}{(e^{\beta\hbar\omega_{\mathbf{k}s}}-1)^2}\\
&+\sum_{\substack{\mathbf{k},s\\ \omega_{\mathbf{k}'s'}\neq\omega_{\mathbf{k}'s'}}}\sum_{\mathbf{k}',s'}\frac{\omega_{\mathbf{k}s}\omega_{\mathbf{k}'s'}}{(\omega_{\mathbf{k}s}-\omega_{\mathbf{k}'s'})^2}\gamma^{ij}_{\mathbf{k}s}(\gamma^{lm}_{\mathbf{k}'s'}-\gamma^{lm})4\hbar^2[C(-\mathbf{k}',s';\mathbf{k}',s)+\bar{D}(-\mathbf{k}',s';\mathbf{k},s)]\\
&\times[C(-\mathbf{k},s;\mathbf{k}',s')+\bar{D}(-\mathbf{k},s;\mathbf{k}',s')]\left[\frac{e^{\beta\hbar\omega_{\mathbf{k}s}}}{(e^{\beta\hbar\omega_{\mathbf{k}s}}-1)^2}+\frac{e^{\beta\hbar\omega_{\mathbf{k}'s'}}}{(e^{\beta\hbar\omega_{\mathbf{k}'s'}}-1)^2}\right]\Bigg] \ .\end{aligned} \tag{52}$$

The first term is of zeroth order. All other terms are of second order. We have omitted terms of higher orders. As in the case of thermal conductivity, we expect the effects of temperature and concentration to show up in the measurements of shear viscosity.

VI. DISCUSSION

We have derived expressions for the various contributions to the thermal conductivity of an impure anharmonic crystal up to second order. Our expressions are new and for the various contributions do not involve any integration over the frequency, which is an advantage over the earlier calculation.[8] Also, the approximations involved in the use of the Dyson equation, Eq. (1), have been avoided.

We have extended our method, based on the double-time Green-function technique of Zubarev,[10] to obtain an expression for the shear viscosity. The derived results for the thermal conductivity and shear viscosity are very cumbersome in their forms. To put them in more useful forms it is necessary to introduce some approximations, as shown below.

In (36), the terms $K_{\rm nd}$, $K_{\rm imp}$, and K_2 are relatively small compared to the others. Using the forms of the coefficients given in Ref. 8, and the symmetry properties of V_3, we obtain

$$K_d=\frac{\pi\hbar^2 k_B\beta^2}{3V}\sum_{\mathbf{k},s}\Bigg\{\omega_{\mathbf{k}s}^2\mathbf{v}_{\mathbf{k}s}^2(1-\beta\hbar\zeta_{\mathbf{k}s}n_{\mathbf{k}s})-2\mathbf{v}_{\mathbf{k}s}^2\bar{C}(-\mathbf{k},s;-\mathbf{k},s)\bar{C}(\mathbf{k},s;\mathbf{k},s)$$
$$-2\sum_{s'\omega_{\mathbf{k}s}=\omega_{\mathbf{k}s'}}\mathbf{v}_{\mathbf{k}s}\cdot\mathbf{v}_{\mathbf{k}s'}[\bar{C}(-\mathbf{k},s;\mathbf{k},s')\bar{C}(-\mathbf{k},s';\mathbf{k},s)-\bar{C}(-\mathbf{k},s;-\mathbf{k},s')\bar{C}(\mathbf{k},s';\mathbf{k},s)]$$
$$+8\sum_{\mathbf{k}',s'}\omega_{\mathbf{k}s}\omega_{\mathbf{k}'s'}\mathbf{v}_{\mathbf{k}s}\cdot\mathbf{v}_{\mathbf{k}'s'}[P_a(-\mathbf{k},s;\mathbf{k}',s')P_b(\mathbf{k},s;-\mathbf{k}',s')-P_b(-\mathbf{k},s;-\mathbf{k}',s')P_a(\mathbf{k},s',\mathbf{k}',s')$$
$$+P_b(-\mathbf{k}',s';\mathbf{k},s)P_a(\mathbf{k}',s';-\mathbf{k},s)$$
$$-P_b(-\mathbf{k}',s';-\mathbf{k},s)P_a(\mathbf{k}',s';\mathbf{k},s)]\Bigg\}\frac{e^{\beta\hbar\omega_{\mathbf{k}s}}}{(e^{\beta\hbar\omega_{\mathbf{k}s}}-1)^2}\,, \tag{53}$$

where

$\zeta_{\mathbf{k}s}=\frac{1}{2}(S_1+S_2+S_V)$, $\bar{C}(\mathbf{k}_1,\mathbf{k}_2)=C(\mathbf{k}_1,\mathbf{k}_2)-\bar{D}(\mathbf{k}_1,\mathbf{k}_2)$,

$$K_c^{(1)}=\frac{3\hbar^3k_B\beta^2}{MNV}\sum_{\mathbf{k},s,\mathbf{k}',s',\mathbf{k}'',s''}\omega_{\mathbf{k}s}\omega_{\mathbf{k}'s'}\omega_{\mathbf{k}''s''}(\boldsymbol{\epsilon}_{\mathbf{k}'s'}\cdot\boldsymbol{\epsilon}_{\mathbf{k}''s''})^2\,|\,V_3(-\mathbf{k},s;\mathbf{k}',s';\mathbf{k}'',s'')\,|^2\tilde{\omega}_{\mathbf{k}s}^2\left[\frac{\omega_{\mathbf{k}'s'}^{(1)}\omega_{\mathbf{k}''s''}^{(1)}}{\tilde{\omega}_{\mathbf{k}'s'}\tilde{\omega}_{\mathbf{k}''s''}}\right]$$
$$\times\left[\frac{1}{[\tilde{\omega}_{\mathbf{k}s}^2-(\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})^2]^2}+\frac{1}{[\tilde{\omega}_{\mathbf{k}s}^2-(\tilde{\omega}_{\mathbf{k}'s'}-\tilde{\omega}_{\mathbf{k}''s''})^2]^2}\right]\frac{e^{\beta\hbar\tilde{\omega}_{\mathbf{k}'s'}}}{(e^{\beta\hbar\tilde{\omega}_{\mathbf{k}'s'}}-1)^2}\frac{e^{\beta\hbar\tilde{\omega}_{\mathbf{k}''s''}}}{(e^{\beta\hbar\tilde{\omega}_{\mathbf{k}''s''}}-1)^2}\,, \tag{54}$$

$$K_c^{(2)}=\frac{3\hbar^3k_B\beta^2}{MNV}\sum_{\mathbf{k},s,\mathbf{k}',s',\mathbf{k}'',s''}\omega_{\mathbf{k}s}\left[\frac{\omega_{\mathbf{k}''s''}^3}{\omega_{\mathbf{k}'s'}}\right](\boldsymbol{\epsilon}_{\mathbf{k}'s'}\cdot\boldsymbol{\epsilon}_{\mathbf{k}''s''})^2\,|\,V_3(-\mathbf{k},s;\mathbf{k}',s';\mathbf{k}'',s'')\,|^2\tilde{\omega}_{\mathbf{k}s}^2\left[\frac{\omega_{\mathbf{k}'s'}^{(2)}\omega_{\mathbf{k}''s''}^{(2)}}{\tilde{\omega}_{\mathbf{k}'s'}\tilde{\omega}_{\mathbf{k}''s''}}\right]$$
$$\times\left[\frac{1}{[\tilde{\omega}_{\mathbf{k}s}^2-(\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})^2]^2}+\frac{1}{[\tilde{\omega}_{\mathbf{k}s}^2-(\tilde{\omega}_{\mathbf{k}'s'}-\tilde{\omega}_{\mathbf{k}''s''})^2]^2}\right]\frac{e^{\beta\hbar\tilde{\omega}_{\mathbf{k}'s'}}}{(e^{\beta\hbar\tilde{\omega}_{\mathbf{k}'s'}}-1)^2}\frac{e^{\beta\hbar\tilde{\omega}_{\mathbf{k}''s''}}}{(e^{\beta\hbar\tilde{\omega}_{\mathbf{k}''s''}}-1)^2}\,, \tag{55}$$

$$K_c^{(3)}=\frac{3\hbar^2k_B\beta^2}{MNV}\sum_{\mathbf{k},s,\mathbf{k}',s',\mathbf{k}'',s''}\omega_{\mathbf{k}''s''}\frac{(\omega_{\mathbf{k}''s''}^2-\omega_{\mathbf{k}'s'}^2)^2}{\omega_{\mathbf{k}s}\omega_{\mathbf{k}'s'}}(\boldsymbol{\epsilon}_{\mathbf{k}'s'}\cdot\boldsymbol{\epsilon}_{\mathbf{k}''s''})^2\,|\,V_3(-\mathbf{k}'',s'';\mathbf{k},s,\mathbf{k}',s')\,|^2\tilde{\omega}_{\mathbf{k}''s''}^2\left[\frac{\omega_{\mathbf{k}s}^{(2)}\omega_{\mathbf{k}'s'}^{(2)}}{\tilde{\omega}_{\mathbf{k}s}\tilde{\omega}_{\mathbf{k}'s'}}\right]$$
$$\times\left[\frac{1}{[\tilde{\omega}_{\mathbf{k}''s''}^2-(\tilde{\omega}_{\mathbf{k}s}+\tilde{\omega}_{\mathbf{k}'s'})^2]^2}+\frac{1}{[\tilde{\omega}_{\mathbf{k}''s''}^2-(\tilde{\omega}_{\mathbf{k}s}-\tilde{\omega}_{\mathbf{k}'s'})^2]^2}\right]\frac{e^{\beta\hbar\omega_{\mathbf{k}'s'}}}{(e^{\beta\hbar\tilde{\omega}_{\mathbf{k}'s'}}-1)^2}\frac{e^{\beta\hbar\tilde{\omega}_{\mathbf{k}''s''}}}{(e^{\beta\hbar\tilde{\omega}_{\mathbf{k}''s''}}-1)^2}\,, \tag{56}$$

$$K_1=\frac{3\hbar^2k_B\beta^2}{V}4\sum_{\mathbf{k},s,\mathbf{k}',s',\mathbf{k}'',s''}|\,\mathbf{J}_{\mathbf{k}s\mathbf{k}'s'\mathbf{k}''s''}\,|^2\,|\,V_3(-\mathbf{k},s;\mathbf{k}',s';\mathbf{k}'',s'')\,|^2\tilde{\omega}_{\mathbf{k}s}^2\left[\frac{\omega_{\mathbf{k}'s'}^{(2)}\omega_{\mathbf{k}''s''}^{(2)}}{\tilde{\omega}_{\mathbf{k}'s'}\tilde{\omega}_{\mathbf{k}''s''}}\right]$$
$$\times\left[\frac{1}{[\tilde{\omega}_{\mathbf{k}s}^2-(\tilde{\omega}_{\mathbf{k}'s'}+\tilde{\omega}_{\mathbf{k}''s''})^2]^2}+\frac{1}{[\tilde{\omega}_{\mathbf{k}s}^2-(\tilde{\omega}_{\mathbf{k}'s'}-\tilde{\omega}_{\mathbf{k}''s''})^2]^2}\right]\frac{e^{\beta\hbar\tilde{\omega}_{\mathbf{k}'s'}}}{(e^{\beta\hbar\tilde{\omega}_{\mathbf{k}'s'}}-1)^2}\frac{e^{\beta\hbar\tilde{\omega}_{\mathbf{k}''s''}}}{(e^{\beta\hbar\tilde{\omega}_{\mathbf{k}''s''}}-1)^2}\,, \tag{57}$$

where

$$\mathbf{J}_{\mathbf{k}s\mathbf{k}'s'\mathbf{k}''s''}=-i\left[\frac{\hbar\omega_{\mathbf{k}s}}{8M\omega_{\mathbf{k}'s'}\omega_{\mathbf{k}''s''}}\right]^{1/2}\frac{1}{3MN^{1/2}V}\Delta(\mathbf{k}+\mathbf{k}'+\mathbf{k}'')\sum_{a,b,c}\epsilon_{\mathbf{k}s}^a\epsilon_{\mathbf{k}'s'}^b\epsilon_{\mathbf{k}''s''}^c\sum_{m,n}\Phi^{abc}(0,\mathbf{x}_m,\mathbf{x}_n)\mathbf{x}_m e^{i(\mathbf{k}\cdot\mathbf{x}_m+\mathbf{k}\cdot\mathbf{x}_n)}$$

with Φ^{abc} as the third-order coupling parameters, and $\mathbf{x}_m$'s as the position vectors of the mth lattice site.

Similarly, (52) reduces to

$$\eta_{ijlm}=\frac{2\pi\hbar^2\beta}{V}\sum_{\mathbf{k},s}\Bigg\{\omega_{\mathbf{k}s}^2\gamma_{\mathbf{k}s}^{ij}(\gamma_{\mathbf{k}s}^{lm}-\gamma^{lm})(1-\beta\hbar\zeta_{\mathbf{k}s}n_{\mathbf{k}s})+4\hbar^2\,|\,\bar{C}(-\mathbf{k},s;\mathbf{k},s)\,|^2$$
$$+\sum_{\substack{s'\\ \omega_{\mathbf{k}s'}=\omega_{\mathbf{k}s}}}\gamma_{\mathbf{k}s}^{ij}(\gamma_{\mathbf{k}s'}^{lm}-\gamma^{lm})2\hbar^2\,|\,\bar{C}(-\mathbf{k},s;\mathbf{k},s')\,|^2$$

$$+\sum_{\substack{\mathbf{k}'s'\\ \omega_{\mathbf{k}'s'}\neq\omega_{\mathbf{k}s}}}\frac{\omega_{\mathbf{k}s}\omega_{\mathbf{k}'s'}}{(\omega_{\mathbf{k}s}-\omega_{\mathbf{k}'s'})^2}[\gamma_k^{ij}(\gamma_{k's'}^{l}-\gamma^{lm})+\gamma_{k's'}^{ij}(\gamma_{ks}^{lm}-\gamma^{lm})]$$

$$\times 4\hbar^2\,|\,C(-\mathbf{k}',s';\mathbf{k},s)+\bar{D}(-\mathbf{k}',s';\mathbf{k},s)\,|^2\Bigg]\frac{e^{\beta\hbar\omega_{\mathbf{k}s}}}{(e^{\beta\hbar\omega_{\mathbf{k}s}}-1)^2}\,, \tag{58}$$

where the generalized Grüneisen parameter is given by[16]

$$\gamma_{ks}^{ij}=-\frac{1}{4M\omega_{\mathbf{k}s}^2}\sum_{l,m}\epsilon_{ks}^{l}\epsilon_{ks}^{m}\sum_{\mu,\nu}[\Phi_{ilm}(\mathbf{x}^\nu,0,\mathbf{x}^\mu)\mathbf{x}_j^\nu+\Phi_{jlm}(\mathbf{x}^\nu,0,\mathbf{x}^\mu)\mathbf{x}_i^\nu]e^{i\mathbf{k}\cdot\mathbf{x}^\mu}\,.$$

Here the Φ_{lmn} are the third-order coupling parameters, $\mathbf{x}^\nu$ is the position vector of the νth atom of mass M, and γ^{ij} is given by (49). The $\mathbf{J}_{\mathbf{k}s\mathbf{k}'s'\mathbf{k}''s''}$ and the γ_{ks}^{ij} have to be separately calculated for each type of atom.

To proceed further we have to make some approximations. For isotropic impurities we may put $D(k_1,k_2)=0$ and as, in general, $V_4 \ll V_3$, we may neglect $\bar{D}$ and V_4 altogether. For $C(k_1,k_2)$ we approximate by

$$|\,C(\mathbf{k}_1,s_1;\mathbf{k}_2,s_2)\,|^2\simeq\left[\frac{M_0}{4\mu N}\right]^2\omega_{\mathbf{k}_1s_1}\omega_{\mathbf{k}_2s_2}(\boldsymbol{\epsilon}_{\mathbf{k}_1s_1}\cdot\boldsymbol{\epsilon}_{\mathbf{k}_2s_2})Nf(1-f)\,|\,\mathbf{k}_1+\mathbf{k}_2\,|^2\,.$$

This vanishes if either $f=0$ or $f=1$, or $\mathbf{k}_1+\mathbf{k}_2=\mathbf{0}$, so that $C(-\mathbf{k},\mathbf{k})=0$. Also, $C(-\mathbf{k},s;\mathbf{k},s')=0$. Thus in this approximation $\omega_{\mathbf{k}}^{(1)}\to\omega_{\mathbf{k}}$, $\omega_{\mathbf{k}}^{(2)}\to\omega_{\mathbf{k}}$, $\tilde{\omega}_{\mathbf{k}}\to\omega_{\mathbf{k}}$, and $\tilde{n}_{\mathbf{k}}\to n_{\mathbf{k}}$. For V_3 we make the approximation given by Klemens[17]

$$|\,V_3(\mathbf{k}_1,s_1;\mathbf{k}_2,s_2;\mathbf{k}_3,s_3)\,|^2=\frac{\lambda_s}{288\omega_{\mathrm{LS}}N}(\omega_{\mathbf{k}_1s_1}\omega_{\mathbf{k}_2s_2}\omega_{\mathbf{k}_3s_3})\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\,. \tag{59}$$

In this approximation $S_2=0$ and

$$\begin{aligned}S_1&\simeq 16\hbar\sum_{k_1\,(\neq k)}\frac{|\,C(-\mathbf{k},s;\mathbf{k}_1,s_1)\,|^2}{(\omega_{ks}^2-\omega_{k_1s_1}^2)}\\&\simeq 16\hbar\left[\frac{M_0}{4\mu N}\right]^2 Nf(1-f)\sum_{\mathbf{k}_1\,(\neq\mathbf{k})}\omega_{\mathbf{k}s}\omega_{\mathbf{k}_1s_1}(\boldsymbol{\epsilon}_{\mathbf{k}s}\cdot\boldsymbol{\epsilon}_{\mathbf{k}_1s_1})^2\frac{\omega_{\mathbf{k}_1s_1}}{(\omega_{\mathbf{k}s}-\omega_{\mathbf{k}_1s_1})}\,|\,\mathbf{k}_1-\mathbf{k}\,|^2\,,\end{aligned} \tag{60}$$

$$S_V\simeq\frac{\hbar\lambda_s}{4\omega_{\mathrm{LS}}N}\sum_{\mathbf{k}_1,s_1,\mathbf{k}_2,s_2}\omega_{\mathbf{k}s}\omega_{\mathbf{k}_1s_1}\omega_{\mathbf{k}_2s_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\left[\frac{\omega_{\mathbf{k}_1s_1}+\omega_{\mathbf{k}_2s_2}}{\omega_{\mathbf{k}s}^2-(\omega_{\mathbf{k}_1s_1}+\omega_{\mathbf{k}_2s_2})^2}+\frac{\omega_{\mathbf{k}_1s_1}-\omega_{\mathbf{k}_2s_2}}{\omega_{\mathbf{k}s}^2-(\omega_{\mathbf{k}_1s_1}-\omega_{\mathbf{k}_2s_2})^2}\right]n_{\mathbf{k}_1s_1}\,. \tag{61}$$

We use the convention $\omega_{-\mathbf{k}s}=\omega_{\mathbf{k}s}$, and $\boldsymbol{\epsilon}_{-\mathbf{k}s}=-\boldsymbol{\epsilon}_{\mathbf{k}s}$, to write

$$\begin{aligned}K_d=\frac{\pi\hbar^2k_B\beta^2}{3V}\sum_{\mathbf{k},s}\Bigg[&\omega_{\mathbf{k}s}^2\mathbf{v}_{\mathbf{k}s}^2(1-\beta\hbar\zeta_{\mathbf{k}s}n_{\mathbf{k}s})-2\mathbf{v}_{\mathbf{k}s}^2\left[\frac{M_0}{4\mu N}\right]^2\omega_{\mathbf{k}s}^2Nf(1-f)4k^2\\&-16\left[\frac{M_0}{4\mu N}\right]^2Nf(1-f)\sum_{\mathbf{k}',s'}\frac{\omega_{\mathbf{k}s}^3\omega_{\mathbf{k}'s'}^3}{(\omega_{\mathbf{k}s}^2-\omega_{\mathbf{k}'s'}^2)^2}\mathbf{v}_{\mathbf{k}s}\cdot\mathbf{v}_{\mathbf{k}'s'}(\boldsymbol{\epsilon}_{\mathbf{k}s}\cdot\boldsymbol{\epsilon}_{\mathbf{k}'s'})^22(k^2+k'^2)\Bigg]\frac{e^{\beta\hbar\omega_{\mathbf{k}s}}}{(e^{\beta\hbar\omega_{\mathbf{k}s}}-1)^2}\,,\end{aligned} \tag{62}$$

$$\begin{aligned}K_0^{(1)}=\frac{3\hbar^3k_B\beta^2}{MNV}\frac{\lambda_s}{288\omega_{\mathrm{LS}}N}&\sum_{\mathbf{k},s,\mathbf{k}',s',\mathbf{k}'',s''}\omega_{\mathbf{k}s}\omega_{\mathbf{k}'s'}\omega_{\mathbf{k}''s''}\Delta(-\mathbf{k}+\mathbf{k}'+\mathbf{k}'')(\boldsymbol{\epsilon}_{\mathbf{k}'s'}\cdot\boldsymbol{\epsilon}_{\mathbf{k}''s''})^2\omega_{\mathbf{k}s}^2\\&\times\left[\frac{1}{[\omega_{\mathbf{k}s}^2-(\omega_{\mathbf{k}'s'}+\omega_{\mathbf{k}''s''})^2]^2}+\frac{1}{[\omega_{\mathbf{k}s}^2-(\omega_{\mathbf{k}'s'}-\omega_{\mathbf{k}''s''})^2]^2}\right]\\&\times\frac{e^{\beta\hbar\omega_{\mathbf{k}'s'}}}{(e^{\beta\hbar\omega_{\mathbf{k}'s'}}-1)^2}\frac{e^{\beta\hbar\omega_{\mathbf{k}''s''}}}{(e^{\beta\hbar\omega_{\mathbf{k}''s''}}-1)^2}\,,\end{aligned} \tag{63}$$

$$\begin{aligned}K_c^{(2)}=\frac{3\hbar^3k_B\beta^2}{MNV}\frac{\lambda_s}{288\omega_{\mathrm{LS}}N}&\sum_{\mathbf{k},s,\mathbf{k}',s',\mathbf{k}'',s''}\omega_{\mathbf{k}s}\omega_{\mathbf{k}''s''}\Delta(-\mathbf{k}+\mathbf{k}'+\mathbf{k}'')(\boldsymbol{\epsilon}_{\mathbf{k}'s'}\cdot\boldsymbol{\epsilon}_{\mathbf{k}''s''})^2\omega_{\mathbf{k}s}^2\\&\times\left[\frac{1}{[\omega_{\mathbf{k}s}^2-(\omega_{\mathbf{k}'s'}+\omega_{\mathbf{k}''s''})^2]^2}+\frac{1}{[\omega_{\mathbf{k}s}^2-(\omega_{\mathbf{k}'s'}-\omega_{\mathbf{k}''s''})^2]^2}\right]\\&\times\frac{e^{\beta\hbar\omega_{\mathbf{k}'s'}}}{(e^{\beta\hbar\omega_{\mathbf{k}'s'}}-1)^2}\frac{e^{\beta\hbar\omega_{\mathbf{k}''s''}}}{(e^{\beta\hbar\omega_{\mathbf{k}''s''}}-1)^2}\,,\end{aligned} \tag{64}$$

$$K_c^{(3)}=\frac{3\hbar^3k_B\beta^2}{MNV}\frac{\lambda_s}{288\omega_{\mathrm{LS}}N}\sum_{\mathbf{k},s,\mathbf{k}',s',\mathbf{k}'',s''}\omega_{\mathbf{k}''s''}^2(\omega_{\mathbf{k}''s''}^2-\omega_{\mathbf{k}'s'}^2)\Delta(-\mathbf{k}''+\mathbf{k}+\mathbf{k}')(\epsilon_{\mathbf{k}'s'}\cdot\epsilon_{\mathbf{k}''s''})^2\omega_{\mathbf{k}''s''}^2$$
$$\times\left[\frac{1}{[\omega_{\mathbf{k}''s''}^2-(\omega_{\mathbf{k}s}+\omega_{\mathbf{k}'s'})^2]^2}+\frac{1}{[\omega_{\mathbf{k}''s''}^2-(\omega_{\mathbf{k}s}-\omega_{\mathbf{k}'s'})^2]^2}\right]$$
$$\times\frac{e^{\beta\hbar\omega_{\mathbf{k}'s'}}}{(e^{\beta\hbar\omega_{\mathbf{k}'s'}}-1)^2}\frac{e^{\beta\hbar\omega_{\mathbf{k}''s''}}}{(e^{\beta\hbar\omega_{\mathbf{k}''s''}}-1)^2}, \tag{65}$$

$$K_1=\frac{3\hbar^2k_B\beta^2}{V}4\frac{\lambda_s}{288\omega_{\mathrm{LS}}N}\sum_{\mathbf{k},s,\mathbf{k}',s',\mathbf{k}'',s''}|J_{\mathbf{k}s\mathbf{k}'s'\mathbf{k}''s''}|^2\omega_{\mathbf{k}s}\omega_{\mathbf{k}'s'}\omega_{\mathbf{k}''s''}\Delta(-\mathbf{k}+\mathbf{k}'+\mathbf{k}'')\omega_{\mathbf{k}s}^2$$
$$\times\left[\frac{1}{[\omega_{\mathbf{k}s}^2-(\omega_{\mathbf{k}'s'}+\omega_{\mathbf{k}''s''})^2]^2}+\frac{1}{[\omega_{\mathbf{k}s}^2-(\omega_{\mathbf{k}'s'}-\omega_{\mathbf{k}''s''})^2]^2}\right]$$
$$\times\frac{e^{\beta\hbar\omega_{\mathbf{k}'s'}}}{(e^{\beta\hbar\omega_{\mathbf{k}'s'}}-1)^2}\frac{e^{\beta\hbar\omega_{\mathbf{k}''s''}}}{(e^{\beta\hbar\omega_{\mathbf{k}''s''}}-1)^2}, \tag{66}$$

$$\eta_{ijlm}=\frac{2\pi\hbar^2\beta}{V}\sum_{\mathbf{k},s}\left[\omega_{\mathbf{k}s}^2\gamma_{\mathbf{k}s}^{ij}(\gamma_{\mathbf{k}s}^{lm}-\gamma^{lm})(1-\beta\hbar\zeta_{\mathbf{k}s}n_{\mathbf{k}s})+4\hbar^2\left[\frac{M_0}{4\mu N}\right]^2\omega_{\mathbf{k}s}^2Nf(1-f)\right.$$
$$\left.\times\sum_{\substack{\mathbf{k}',s'\\ \omega_{\mathbf{k}s}\neq\omega_{\mathbf{k}'s'}}}\frac{\omega_{\mathbf{k}s}\omega_{\mathbf{k}'s'}}{(\omega_{\mathbf{k}s}-\omega_{\mathbf{k}'s'})^2}[\gamma_{\mathbf{k}s}^{ij}(\gamma_{k's'}^{lm}-\gamma^{lm})+\gamma_{k's'}^{ij}(\gamma_{\mathbf{k}s}^{lm}-\gamma^{lm})]\,|\mathbf{k}-\mathbf{k}'|^2\right]\frac{e^{\beta\hbar\omega_{\mathbf{k}s}}}{(e^{\beta\hbar\omega_{\mathbf{k}s}}-1)^2}. \tag{67}$$

The factors involving exponentials can be expanded in power series when β is small in the high-temperature limit. This will further simplify the expressions. Further progress can only be made if we know the wave-vector frequency relation for the substance of interest and then we can use these formulas for numerical calculations.

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