Universal high-temperature saturation in phonon and electron transport

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High-temperature electrical conductivity σ of metals and thermal conductivity κ of insulators exhibit very similar saturation effects when the mean free path l approaches the lattice constant a. Band-mixing effects are shown to be an important factor in this regime. We predict that TlBr and TlCl should exhibit saturation effects in κ, similar to those seen in CuCl.

High-T transport in the phonon or electron "gas" in a solid has a very simple form. Boltzmann theory[1] gives an inelastic collision rate $1/\tau$ scaling as $\langle u^2 \rangle \propto T$ where u is the vibrational amplitude. The conductivity then scales as T^{-1}. This is true both for electrical conductivity σ in metals (where the inelastic mechanism is electron-phonon scattering) and for heat conductivity κ in insulators (where the mechanism is phonon-phonon scattering). Figure 1 shows the success of this picture for good conductors like Cu and Si.[15] Also shown is the crossover to T-independent behavior ("minimum" conductivity) seen at high T in strong-scattering materials like V$_3$Si (Ref. 16) and CuCl. The crossover occurs in all electrical conductors with $\sigma \lesssim 2 \times 10^6 \ \Omega^{-1} \mathrm{m}^{-1}$ and in thermal conductors with $\kappa \lesssim 0.5$—5.0 W/mK. The striking similarity of the crossover in σ and κ has not previously been noticed. This crossover cannot be described by Boltzmann theory since $\langle u^2 \rangle \propto T$ is inescapable. The crossover correlates with short inelastic mean free paths $l \rightarrow a$ where a is a lattice constant. In this regime, quasiparticles are not well defined (i.e., $\vec{Q}$ is not a good quantum number; this is seen directly in CuCl by neutron scattering[14]) and the gas analogy implicit in Boltzmann theory is invalid.

There is a large literature[17] on the problem of minimum electronic conductivity at high T, and it is clear that a quantitative theory does not yet exist. The corresponding phonon problem has been discussed phenomenologically by Slack,[18,19] but no microscopic theory has been pro-
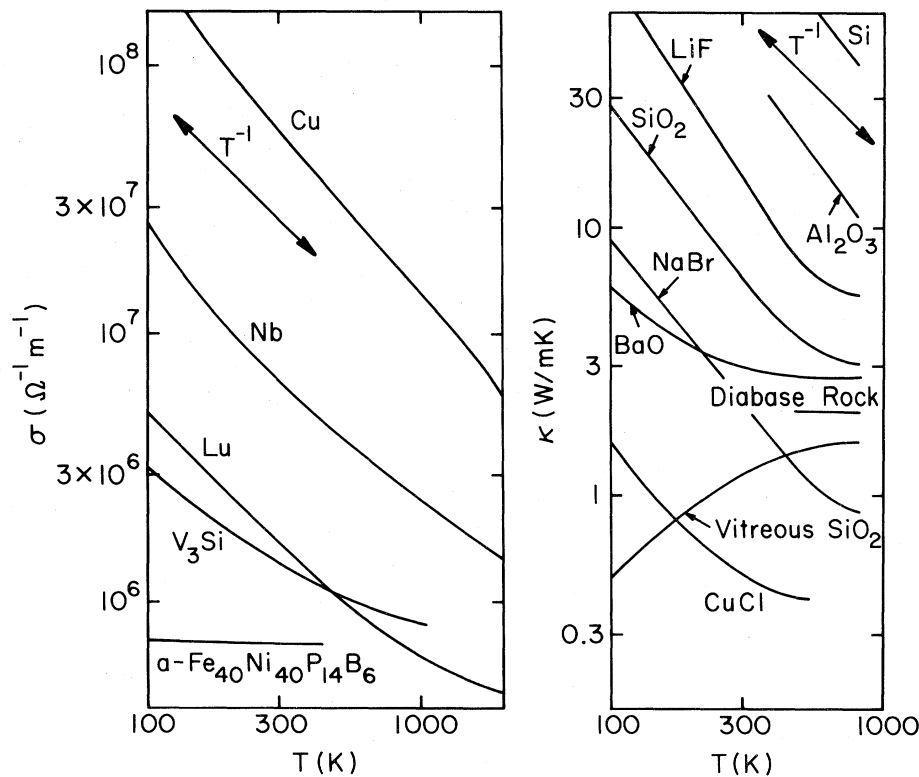

FIG. 1. Conductivities vs temperature. All scales are logarithmic. Data for κ are not shown above 800 K, where radiative heat transfer begins to be noticeable. The sources of data are as follows: Cu, Ref. 2; Nb, Ref. 3; Ln, Ref. 4; Y$_3$Si, Ref. 5; a-Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$, Ref. 6; Si, Ref. 7; Al$_2$O$_3$, Ref. 8; LiF and NaBr, Ref. 9; a-SiO$_2$, Ref. 10; BaO, Ref. 11; diabase rock, Ref. 12; vitreous SiO$_2$, Ref. 13; CuCl, Ref. 14.

posed. The high-T problem is in large part distinct from the question of minimum conductivity at low T, which also has a large literature.[20] The distinction is discussed in detail later in this paper. The main purpose of this paper is to emphasize that the crossover and the regime of minimum conductivity are simple, universal, and unexplained. The similarity of σ and κ has some immediate consequences which help clarify the problem in both fields. The second purpose of this paper is to emphasize that interband effects[21] are numerically important and have the right features to explain the effect.

Quite a satisfactory phenomenological model for the crossover is provided by the "shunt-resistor" equations[22,19]

$$\sigma = \sigma_B + \sigma_{\min}, \quad \sigma_{\min} \cong e^2/\hbar a , \tag{1}$$

$$\kappa = \kappa_B + \kappa_{\min}, \quad \kappa_{\min} \cong k_B^2 \Theta_D/\hbar a , \tag{2}$$

where σ_B and κ_B are the electrical and thermal conductivities predicted by Boltzmann theory.[23] The minimum conductivity formulas can be constructed from simple dimensional arguments. The intuitive picture of Kittel[24] and Ioffe and Regel[25] replaces the mean free path in the gas-theory formula by a minimum sensible value (either the wavelength or the lattice constant).

Observation 1. The dimensional argument cannot specify the sign of the effect in Eqs. (1) and (2). This is dramatically demonstrated by the predicted behavior of σ at $T=0$ in dirty metals. As the mean free path is decreased by increased static disorder, an Anderson transition[26] occurs to the localized regime where $\sigma=0$. Most theories and also recent experiments[27] describe this as a continuous transition, and Götze[28] has emphasized that (except in a narrow critical region) the transition is well described by Eq. (1) *with a negative value* of $\sigma_{\min}$, rather than the positive value needed at high T. The importance of this observation is to dispel the notion that an elementary argument exists to justify Eqs. (1) and (2). Dimensional arguments correctly give the value of σ at which a failure of gas theory occurs, but do not explain why the high-T behavior is as simple as Eqs. (1) and (2).

Observation 2. The explanation of the high-T behavior must apply to both σ and κ and thus cannot rely on features specific to electrons or to phonons. For example, theories involving $k_B T/\epsilon_F$ corrections[29] ("Fermi smearing") or exchange scattering[30] can be ruled out because there is no phonon analog. The phenomenon seems to be a general property of waves propagating in a medium with vibrational disorder, and does not depend on whether the wave is itself vibrational or simply coupled to the vibrations.

Observation 3. It is not yet known whether the time dependence of thermal disorder is a necessary or a peripheral aspect. In Boltzmann transport the time dependence is peripheral at high T. One can treat the disorder as static, calculate the corresponding *elastic* scattering rate from the adiabatically distorted lattice, and perform a thermal ensemble average. The fact that the actual scattering is inelastic (because of time dependence of u) gives only a negligible correction if $T > \Theta_D$. However, in the case $l \sim a$, the possibility must be considered that the instantaneous eigenstates of the adiabatically distorted lat-

tice are localized. If these states are used as a basis for constructing a transport theory, then time-dependent (inelastic) effects are crucial for allowing conduction to occur. Two facts suggest that the instantaneous eigenstates are not localized. First, no one has shown how the temperature cancels out of the high-T problem if the role of vibrational disorder is to cause hopping conduction in instantaneously localized states. Second, in metals which follow Eq. (1) at high T, it is usually surprisingly easy to obtain $\sigma \rightarrow \sigma_{\min}$ at $T=0$ by alloying or radiation damage. If instantaneous states are localized at high T, then they should be localized at $T=0$ in dirty samples with l correspondingly small. Experimentally, $\sigma < \sigma_{\min}$ seems hard to achieve, and $\sigma \rightarrow 0$ has never been demonstrated. Thus it seems probable that these metals are quite far from an Anderson transition and obey Eq. (1) with a *positive* value of $\sigma_{\min}$ even at $T=0$. Localization appears not to occur for any physically realizable degree of disorder.

Observation 4. Interband effects are very important in metals like V$_3$Si, where the typical band separation $\Delta \epsilon$ is $\sim \frac{1}{3}$ eV, and $\hbar/\tau$ is as large as $\Delta \epsilon$ at $T \sim \Theta_D$. It has been shown[21] that this gives rise to a new mechanism of electronic conduction distinct from either hopping or gaslike quasiparticle drift. For weak scattering this process occurs in parallel with quasiparticle drift, and provides a natural picture of the parallel resistor of Eq. (1). The time dependence of u is peripheral in this theory; the same effects occur at $T=0$ if $1/\tau$ is caused by static disorder. This explains the difficulty of achieving $\sigma < \sigma_{\min}$ at $T=0$. We now show that interband effects of an exactly analogous kind occur in phonon conduction.

The possibility of interband contributions to σ arises because the electrical current operator $\vec{j}$ has interband matrix elements $-(e/m)\langle \vec{k}n \,|\, \vec{p} \,|\, \vec{k}n' \rangle$. Boltzmann theory considers only the diagonal part $-e\vec{v}_{\vec{k}n}$ which describes quasiparticle drift. In the absence of collisions, the off-diagonal part gives no in-phase current unless the $\vec{E}$ field oscillates on resonance with an interband transition. The heat-current operator $\vec{S}$ for an insulator was derived by Hardy:[31]

$$\vec{S} = \frac{1}{2} \sum_{\vec{k}} \sum_{j,j'} (\omega_{\vec{k}j} + \omega_{\vec{k}j'}) \vec{v}_{\vec{k}jj'} a^\dagger_{\vec{k}j} a_{\vec{k}j} + \vec{S}_2 + \vec{S}_3 , \tag{3}$$

$$(v_{\vec{k}jj'})_x = \frac{1}{2} (\omega_{\vec{k}j} \omega_{\vec{k}j'})^{-1/2} \langle \vec{k},j \,|\, \partial\hat{\phi}(\vec{k})/\partial k_x \,|\, \vec{k},j' \rangle , \tag{4}$$

where $a^\dagger$ and a are phonon creation and destruction operators and the polarization vectors $|\, \vec{k},j \rangle$ are eigenvectors of the dynamical matrix $\hat{\phi}(\vec{k})$ with eigenvalue $\omega_{\vec{k}j}^2$. From the Feynman theorem it is clear that the diagonal parts of $\vec{v}_{\vec{k}jj'}$ are the group velocities $\vec{v}_{\vec{k}j} = \partial\omega_{\vec{k}j}/\partial\vec{k}$. The off-diagonal velocities are not small. Results for v_x are shown in Fig. 2 for Ge phonons propagating in the [100] direction. At $\vec{k} = (2\pi/a)(1,0,0)$, we find the value $\langle \text{TA} \,|\, v_x \,|\, \text{TO} \rangle \sim 4 \times 10^3$ m/s, which is larger than any other matrix element of v_x in that direction except near $\vec{k} = \vec{0}$ where $\langle \text{LA} \,|\, v_x \,|\, \text{LA} \rangle \sim 5 \times 10^3$ m/s is the LA sound velocity. The term $\vec{S}_2$ is similar to the first term of (3) but
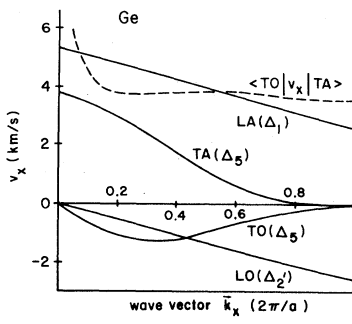
FIG. 2. Matrix elements $(v_{\vec{k}jj'})_x$ of v_x for Ge phonons in the [100] direction. All off-diagonal matrix elements vanish by symmetry except for the 2×2 blocks of $\langle TA | v_x | TO \rangle$. By a unitary transformation these blocks are given the form of a constant (shown as the dashed line) times the unit matrix. Solid lines are the diagonal elements $(v_{\vec{k}jj})_x$ which are identical to the phonon group velocities. Dynamical matrix chosen was Weber's band change model (Ref. 32).

has operators $a^\dagger a^\dagger$ and aa, while the term $\vec{S}_3$ contains trilinear operators $a^\dagger aa$, etc., coming partly from the harmonic Hamiltonian, and partly from anharmonic perturbations. We have analyzed only the effects of the first term of Eq. (3).

Following the procedure of Ref. 21, we define a generalized distribution function which is a $3v \times 3v$-dimensional matrix in the branch index (jj'), where v is the number of atoms per unit cell:

$$N_{\vec{k}jj'} \equiv \mathrm{tr}(\rho a^\dagger_{\vec{k}j} a_{\vec{k}j'})$$

$$= (n_{\vec{k}j} + \phi_{\vec{k}j})\delta_{jj'} + \psi_{\vec{k}jj'}(1-\delta_{jj'}) . \tag{5}$$

Here ϕ and ψ are the diagonal and off-diagonal parts of the deviation from the equilibrium Bose function $n_{\vec{k}j}$. Let us represent $N_{\vec{k}jj'}$ as a column vector $|N\rangle$ with the diagonal parts in the uppermost $3vN$ entries and the off-diagonal elements in the remaining $3v(3v-1)N$ places, where N is the number of $\vec{k}$ vectors in the Brillouin zone. The linearized truncated equation of motion for N is

$$\begin{bmatrix} P & R \\ R^\dagger & Q-i\Omega \end{bmatrix} \begin{bmatrix} \phi \\ \psi \end{bmatrix} = -\frac{|\vec{\nabla}T|}{T} \begin{bmatrix} X \\ Y \end{bmatrix} \tag{6}$$

which generalizes the Peierls-Boltzmann equation $P\phi = -|\vec{\nabla}T/T|X$ in the presence of a thermal gradient $\vec{\nabla}T$. We have derived an explicit form for the scattering operators P,Q,R in the case of third-order anharmonic interactions. The operator P agrees with the usual theory.[1] The other parts are quite complicated and are given in the Appendix. As in Ref. 21, Ω is an "inertial" term which suppresses interband fluctuations,

$$(\Omega\psi)_{\vec{k}jj'} = \hbar(\omega_{\vec{k}j} - \omega_{\vec{k}j'})\psi_{\vec{k}jj'} . \tag{7}$$

The driving terms X,Y were found by the method of Ref. 33. The off-diagonal part is

$$Y_{\vec{k}jj'} = \frac{\omega_{\vec{k}j} + \omega_{\vec{k}j'}}{2} v_{\vec{k}jj'} \frac{n_{\vec{k}j'} - n_{\vec{k}j}}{\omega_{\vec{k}j'} - \omega_{\vec{k}j}} \tag{8}$$

while the diagonal part X_{kj} is as usual $\omega_{\vec{k}j} v_{\vec{k}j} \partial n_{\vec{k}j} / \partial \omega_{\vec{k}j}$, plus a correction $X^{(1)}$ due to interactions. These are further described in the Appendix.

The thermal conductivity $\kappa = -\mathrm{tr}(\rho S_x)/\nabla_x T$ can now be calculated from the solution of Eq. (6). For example, in semiclassical approximation $(R = Q = X^{(1)} = 0)$ the formal result is

$$\kappa_B = \frac{1}{T} \sum_{k,k'} \hbar\omega_k v_{kx} (P^{-1})_{kk'} \omega_{k'} v_{k'x} (\partial n / \partial \omega_{k'}) , \tag{9}$$

where k is short for $(\vec{k},j)$. In the relaxation-time approximation, $(P^{-1})_{kk'} = -\tau\delta_{kk'}$, the standard formulas are recovered. The next-order corrections to Eq. (9) are easily found, and can be simply transcribed from the results of Ref. 21. These correction terms differ from (9) in two ways: (1) they have additional factors such as $R\Omega^{-1}$ which is of order $1/\omega_D\tau$ or a/l, and (2) all but one term has one or both of the diagonal velocities $v_{\vec{k}j}$ replaced by $v_{\vec{k}jj'}$ with $j' \neq j$. When the first corrections are added to Eq. (9), the resulting theory has exactly the form and magnitude of Eq. (2).

For optical branches, $\vec{v}_{\vec{k}j}$ is small while $\vec{v}_{\vec{k}jj'}$ has terms of order $v_s \sim \omega_D a/2\pi$. This helps to explain an interesting aspect of Slack's semiempirical formulas[18] for κ_{min}. For acoustic branches, the contribution to κ_{min} is just what one expects from kinetic theory with $l \sim \lambda$, and v the sound velocity. For optical branches, however, he assigns a velocity $\sim \omega_D a/2\pi$ rather than the much smaller group velocity. In a very successful shunt-resistor fit to data for CuCl at various pressures[19] it was found that the three optical branches carry about half the heat in the saturated limit. This is very surprising since the three acoustic branches have much larger velocities. The interband theory gives a detailed mechanism for this result.

Srivastava[34] and others have earlier estimated the influence on κ of off-diagonal parts of the heat-current operator $\vec{S}$ [Eq. (3)]. There is a close connection between these approaches and ours, but an even more important difference. The contribution κ_{nd} found in Ref. 21 from nondiagonal parts of $\vec{S}$ is smaller than the diagonal part κ_d by two powers of the small parameter $(\omega_D\tau)^{-1}$ or (a/l), whereas our first correction is smaller by only one power. Apparently these authors have omitted scattering processes which couple the diagonal and off-diagonal parts of the nonequilibrium distribution, or equivalently, have not fully exploited the matrix nature of the phonon self-energy $\pi_{jj'}(Q,\omega)$. An exactly similar discrepancy exists in the electron problem between the phenomenological treatment of Garik and Ashcroft[35] and the microscopic treatment of Ref. 21. A phenomenological method of obtaining first- instead of second-order corrections in powers of (a/l) is given in Ref. 36.

The present theory of interband effects is far from complete. The basic defect is that, like the usual Boltzmann theories, it is based on a representation in which $\vec{k}$ is a good quantum number. In the regime $a/l \sim 1$, additional

nondiagonal parts $N_{\vec{k}j,\vec{k}'j'}$ of the distribution function would be needed, and one would not expect the theory to be manageable. The virtue of the present theory is that it shows clearly the importance of the interband mechanism, and should correctly describe the regime where the correction to Boltzmann theory is small.

The close analogy between electron and phonon transport may provide insights and simplifications in future work. For example, computer simulations of electrical[37] and heat[38,39] currents have been made. Most of this work involves only static disorder, but Payton et al.[38] included anharmonic phonon scattering as an additional ingredient. They found a regime where the anharmonic interactions enhanced the heat current beyond what it would have been for the statically disordered lattice. There is probably no way to compare this result directly with experimental thermal conductivity. However, electrical conductivity of metals has the simplification that the conductivity of the statically disordered lattice is to good approximation independent of T and measurable at $T=0$. The enhanced currents found by Payton and Visscher probably correspond to the Mooij correlation,[40] i.e., the tendency for highly resistive metallic alloys to have negative temperature coefficients of resistivity.

In the case of metals, it is relatively safe to predict that whenever ρ at room temperature exceeds 80 $\mu\Omega$ cm, the measured resistivity will be only weakly T dependent. For insulators, it is harder to predict the behavior simply because Eq. (2) for $\kappa_{\min}$ varies quite a lot between materials. However, we wish to predict that TlBr and TlCl should exhibit saturation effects in κ at 300 K and above. This prediction is based on the neutron measurements of phonon frequencies[41] which show strong T-dependent broadening of the phonon lines. Except for some data on mixed crystals[42] and for TlBr in a limited range of temperature[43] there seem to be no measurements of $\kappa(T)$ for these materials. The value measured in Ref. 43 for TlBr at 316 K is 0.59 W/mK, close to the value 0.3 W/mK estimated for $\kappa_{\min}$ from Eq. (2), or the value 0.49 W/mK which we estimate from Slack's more sophisticated formulas.[18]

Our main conclusions are that phonon and electron minimum conductivities are very much alike. The effects of band mixing are large when $l \sim a$ and seem to us a necessary ingredient in any complete model. Mechanisms which are special to electrons or to phonons can be ruled out.

APPENDIX

This appendix contains derivations of Eqs. (6)—(9). It is convenient to rewrite Eq. (6) in the form

$$(\hat{K}-i\hat{\Omega})\Phi=-|\vec{\nabla}T/T|Z,\qquad\text{(A1)}$$

where Φ is the deviation of the distribution function N from equilibrium,

$$N_{\vec{k}jj'}=n_{\vec{k}j}\delta_{jj'}+\Phi_{\vec{k}jj'},\qquad\text{(A2)}$$

i.e., Φ is the column vector with elements (ϕ,ψ) in Eq. (6). The scattering operator is $\hat{K}$, the driving term with elements (X,Y) in Eq. (6) is denoted Z, and $\hat{\Omega}$ will be defined later.

The density matrix is written as

$$\rho=\rho_0+\rho_1,\qquad\text{(A3)}$$

where ρ_0 is the equilibrium density matrix $e^{-\beta\mathscr{H}_0}$ and ρ_1 corresponds to the first order (in $|\nabla T/T|$) deviation from equilibrium. We shall use an abbreviated notation for the phonon quantum numbers such as $1=(\vec{k},j)$, $1'=(\vec{k},j')$, and $-1=(-\vec{k},j)$. Thus, for example, $\Phi_{11'}\equiv\mathrm{tr}(\rho_1 a_1^\dagger a_{1'})$. The heat current, as given by Eqs. (3) and (4), is

$$\vec{J}=\mathrm{tr}(\rho\vec{S})=\tfrac{1}{2}\sum_{1,1'}(\omega_1+\omega_{1'})v_{11'}\Phi_{11'}+\vec{J}_2+\vec{J}_3.\qquad\text{(A4)}$$

$\vec{J}_2$ and $\vec{J}_3$ correspond to the $\vec{S}_2$ and $\vec{S}_3$ operators. As in Refs. 21 and 33, we use Kohn and Luttinger's method[44] of writing the Liouville equation of the density matrix of a steady-state system,

$$-i\hbar\frac{\partial\rho}{\partial t}=[\mathscr{H}_T,\rho]=0,\qquad\text{(A5)}$$

$$\mathscr{H}_T=\mathscr{H}_h+\mathscr{H}_a+\vec{\mathscr{H}}_\beta,\qquad\text{(A6)}$$

$$\mathscr{H}_h=\sum_1\hbar\omega_1(a_1^\dagger a_1+\tfrac{1}{2}),\qquad\text{(A7)}$$

$$\mathscr{H}_a=\frac{1}{3!}\sum_{1,2,3}V(1,2,3)(a_1^\dagger-a_{-1})$$
$$\times(a_2^\dagger-a_{-2})(a_3^\dagger-a_{-3}).\qquad\text{(A8)}$$

Here $\vec{\mathscr{H}}_\beta$ is the effective driving perturbation derived[33,45] for a system under a constant thermal gradient, which is assumed to reach local thermal equilibrium. Thus a space-dependent inverse temperature $\beta(x)$ is defined.

To first order in $|\vec{\nabla}\beta|/\beta$ our system is equivalent to a lattice in a constant temperature $1/\beta$ with a perturbing Hamiltonian[45]

$$\vec{\mathscr{H}}_\beta=\int_0^\beta d\lambda\, e^{-\lambda\mathscr{H}_h}\mathscr{H}_\beta e^{\lambda\mathscr{H}_h},\qquad\text{(A9)}$$

$$\mathscr{H}_\beta=\frac{\vec{\nabla}\beta}{\beta}\cdot\int dx\,\vec{x}\sum_i\Delta_1(x-x_i)\frac{P_i^2}{2m_i}$$
$$+\tfrac{1}{2}\sum_j\phi_{\alpha\beta}(i,j)Q_{i\alpha}Q_{j\beta},\qquad\text{(A10)}$$

where $\Delta(x)$ is a δ function broadened in space to the degree necessary to define a local temperature.[31] The force constants are denoted by $\vec{\phi}(i,j)$ and the lattice momentum and coordinate $\vec{P}$ and $\vec{Q}$ are

$$P_{i\alpha} = iN^{-1/2} \sum_{\vec{k},j} (\tfrac{1}{2}\hbar m_i \omega_{\vec{k}j})^{1/2} e_\alpha(i,\vec{k}j)$$

$$\times (a^\dagger_{\vec{k}j} + a_{-\vec{k}j}) e^{i\vec{k}\cdot\vec{x}_i} , \qquad (A11)$$

$$Q_{i\alpha} = N^{-1/2} \sum_{\vec{k},j} (\hbar/2m_i\omega_{\vec{k}j})^{1/2} e_\alpha(i,\vec{k}j)$$

$$\times (a^\dagger_{\vec{k}j} - a_{\vec{k}j}) e^{i\vec{k}\cdot\vec{x}_i} . \qquad (A12)$$

Expanding Eq. (A5) in powers of $|\vec{\nabla}T|/T$ yields

$$i[\mathscr{H}_h, \rho_0] + i[\mathscr{H}_a, \rho_0] = 0 , \qquad (A13)$$

$$i[\mathscr{H}_h, \rho_1] + i[\mathscr{H}_{ah}, \rho_1] + i[\vec{\mathscr{H}}_\beta, \rho_0] = 0 . \qquad (A14)$$

Multiplying (A14) by $a^\dagger_1 a_{1'}$, taking the trace and using its cyclic property we obtain

$$i\,\mathrm{tr}(\rho_1[a^\dagger_1 a_{1'}, \mathscr{H}_h]) + i\,\mathrm{tr}(\rho_1[a^\dagger_1 a_{1'}, \mathscr{H}_{ah}])$$

$$+ i\,\mathrm{tr}(\rho_0[a^\dagger_1 a_{1'}, \vec{\mathscr{H}}_\beta]) = 0 . \qquad (A15)$$

The three terms represent the "inertial," "scattering," and "driving" terms, respectively. The form of the inertial term is

$$i\,\mathrm{tr}(\rho_1[a^\dagger_1 a_{1'}, \mathscr{H}_h]) = i\hbar(\omega_1 - \omega_{1'})\Phi_{11'}$$

$$\equiv i(\hat{\Omega}\Phi)_{11'} , \qquad (A16)$$

$$\Omega_{11',22'} = \hbar(\omega_1 - \omega_{1'})\delta_{12}\delta_{1'2'} . \qquad (A17)$$

The word inertial has less significance here than it has in the electron problem.[21] The significance of the inertial term is that it suppresses interband fluctuations unless the energy mismatch $\omega_1 - \omega_{1'}$ is small. The driving term is

$$i\,\mathrm{tr}(\rho_0[a^\dagger_1 a_{1'}, \vec{\mathscr{H}}_\beta]) = -\frac{|\vec{\nabla}T|}{T} Z_{11'} , \qquad (A18)$$

$$\vec{\mathscr{H}}_\beta = i\frac{\vec{\nabla}T}{T} \sum_{2,2'} (e^{\beta\hbar(\omega_2-\omega_{2'})} - 1)$$

$$\times [(\omega_2 + \omega_{2'})/(\omega_2 - \omega_{2'})^2]\vec{v}_{22'} a^\dagger_2 a_{2'} , \quad (A19)$$

where the velocity $\vec{v}_{\vec{k}jj'}$ is defined in Eq. (4). As in Eq. (6), we now use X to denote the band-diagonal (or intraband) part of Z, and Y to denote the interband part:

$$X_{11} = \omega_1 \left[\frac{d\omega}{dk}\right]_1 \left[\frac{dn}{d\omega}\right]_1 , \qquad (A20)$$

$$Y_{11'} = \frac{\omega_1 + \omega_{1'}}{2} v_{11'} \frac{n_1 - n_{1'}}{\omega_1 - \omega_{1'}} . \qquad (A21)$$

The scattering term will yield the tetradic matrix $\hat{K}$ which operates on Φ. With the use of Eq. (A8),

$$\sum_{2,2'} K_{11'22'}\Phi_{22'} = i\,\mathrm{tr}(\rho_1[a_1 a_{1'}, \mathscr{H}_{ah}])$$

$$= \frac{i}{3!} \sum_{2,3,4} V(2,3,4)\mathrm{tr}(\rho_1[a^\dagger_1 a^\dagger_3 a_4 \delta_{1',2} + a^\dagger_1 a_3 a_4 \delta_{1',2} + \cdots]) , \qquad (A22)$$

where the ellipsis represents other unspecified trilinear terms. Evaluating the traces of a trilinear term requires another equation, which is given by multiplying Eq. (A14) by the trilinear operator and taking the trace

$$\mathrm{tr}(\rho_1[a^\dagger_1 a^\dagger_2 a_3, \mathscr{H}_h]) + \mathrm{tr}(\rho_1[a^\dagger_1 a^\dagger_2 a_3, \mathscr{H}_{ah}])$$

$$+ \mathrm{tr}(\rho_0[a^\dagger_1 a^\dagger_2 a_3, \vec{\mathscr{H}}_\beta]) = 0 . \qquad (A23)$$

The third term vanishes since ρ_0 is diagonal in the number representation. Using Eq. (A13), ρ_1 may be replaced by $\rho = \rho_0 + \rho_1$ in the remaining two terms. But, in the first term, the part involving ρ_0 clearly vanishes. Working out commutators, Eq. (A23) becomes

$$\hbar(\omega_1 + \omega_2 - \omega_3 + i\eta)\mathrm{tr}(\rho_1 a^\dagger_1 a^\dagger_2 a_3)$$

$$= -\frac{1}{3!} \sum_{a,b,c} V(a,b,c)\mathrm{tr}(\rho[-\delta_{2,-b} a^\dagger_1 a^\dagger_a a_3 a_c + \cdots]) , \qquad (A24)$$

where the ellipsis represents the following unspecified terms: 16 other terms with two $a^\dagger$'s and two a's, and other terms with $a^\dagger a^\dagger a^\dagger a$ and $aaaa^\dagger$. As usual, an infinitesimal $i\eta$ is added to give the correct analytic properties. This is most clearly understood when the temperature gradient is oscillatory, $e^{-i\omega t}$. To simplify the formalism at this point we neglect the last two kinds of terms, which correspond to interband distribution functions, that lead to additional channels carrying heat via $\vec{S}_2$ and $\vec{S}_3$ operators described in Eq. (3).

We now decouple the four operator averages of Eq. (A24) into products of two operator averages, taking all "contractions" as in Wick's theorem, to obtain a closed equation. This decoupling is accurate to second order in V. Thus, for instance,

$$\mathrm{tr}(\rho a^\dagger_1 a^\dagger_{1'} a_2 a_{2'}) \cong \mathrm{tr}(\rho a^\dagger_1 a_{2'})\mathrm{tr}(\rho a^\dagger_{1'} a_2) + \mathrm{tr}(\rho a^\dagger_1 a_2)\mathrm{tr}(\rho a^\dagger_{1'} a_{2'})$$

$$= \delta_{12} n_1 \Phi_{1'2'} + \delta_{12'} n_1 \Phi_{1'2} + \delta_{1'2'} n_{1'} \Phi_{12} + \delta_{1'2} n_{1'} \Phi_{12'} + O((|\vec{\nabla}T|/T)^2) . \qquad (A25)$$

After contracting the averages we arrive at the form of the scattering operator K,

$$(\hat{K}\Phi)_{11'} = -\frac{i}{\hbar} \sum_{2,3,2',3'} \frac{V(1,2,3)V(3',2',1')}{\omega_{1'}-\omega_2-\omega_3+i\eta}[(n_{2'}+n_{3'})\Phi_{11'}+(n_{1'}-n_{3'})\Phi_{22'}+(n_{1'}-n_{2'})\Phi_{33'}]-(1\leftrightarrow1',\ i\eta\rightarrow-i\eta)$$

$$-\frac{2i}{\hbar} \sum_{2,3,2',3'} \frac{V(1,2,3)V(3',2',1')}{\omega_{1'}+\omega_2-\omega_3+i\eta}[(n_{2'}-n_{3'})\Phi_{11'}+(n_{1'}-n_{3'})\Phi_{22'}-(n_{1'}+n_{2'}+1)\Phi_{33'}]-(1\leftrightarrow1',\ i\eta\rightarrow-i\eta)\ .$$

$$(A26)$$

To get this in the form of Eq. (6) with interband and intraband parts separated, it is convenient to define the interband projection operator,

$$(\hat{\Delta})_{11'22'} = \delta_{11'}\cdot\delta_{22'}\ .\tag{A27}$$

The elements of the matrix $\hat{K}$ in Eq. (6) are

$$\hat{P} = \hat{\Delta}\hat{K}\Delta\ ,\tag{A28}$$

$$\hat{R} = \hat{\Delta}\hat{K}(1-\hat{\Delta})\ ,\tag{A29}$$

$$\hat{Q} = (1-\hat{\Delta})\hat{K}(1-\hat{\Delta})\ .\tag{A30}$$

$\hat{P}$ is easily recognized as the usual Boltzmann scattering term for cubic anharmonicity[1]

$$(P\Phi)_{11} = -\frac{2\pi}{\hbar} \sum_{2,3} |V(1,2,3)|^2\delta(\omega_1-\omega_2-\omega_3)[(n_2+n_3)\phi_1+(n_1-n_3)\phi_2+(n_1-n_2)\phi_3]$$

$$-\frac{2\pi}{\hbar} \sum_{2,3} |V(1,2,3)|^2\delta(\omega_1+\omega_2-\omega_3)[(n_2-n_3)\phi_1+(n_1-n_3)\phi_2-(n_1+n_2+1)\phi_3]\ .\tag{A31}$$

The first correction to the Boltzmann result κ_B [Eq. (9)] is of order $\kappa_B(\Delta\omega\tau)^{-1}$, where $\Delta\omega$ is a typical interband frequency separation and $\hbar/\tau$ the average magnitude of the scattering operator $\hat{K}$. Thus as in Refs. 21 and 33,

$$\kappa = \kappa_B + \kappa^{(0)}\ ,\tag{A32}$$

$$\kappa^{(0)} = \frac{i}{T} \sum_{1} \hbar\omega_1 v_1[(-\hat{P}^{-1}\hat{R}\hat{\Omega}^{-1}Y)_1+(P^{-1}R\Omega^{-1}R^{-1}P^{-1}X)_1] - \frac{i}{T} \sum_{1,1'} \hbar\left[\frac{\omega_1+\omega_{1'}}{2}\right]v_{11'}(\hat{\Omega}^{-1}\hat{R}^{\dagger}\hat{P}^{-1}X)_{11'}\ .\tag{A33}$$

By inspecting the magnitude of the correction $\kappa^{(0)}$, it is seen that Eq. (A32) has the form of the shunt-resistor formula, Eq. (2).

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[1]For electrons, this is the Bloch-Boltzmann equation [F. Bloch, Z. Phys. 52, 555 (1928)] which couples electrons to thermal phonons; for phonons, this is the Peierls-Boltzmann equation [R. E. Peierls, Ann. Phys. (Leipzig) 3, 1055 (1929)] which couples phonons to each other via anharmonic terms. See, for example, J. M. Ziman, *Electrons and Phonons* (Oxford University, London, 1960).

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