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Lattice Thermal Conductivity[*]

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The lattice thermal conductivity for monatomic crystals is discussed for high temperatures, above and around the Debye temperature. While this problem cannot be treated in a suitable way by conventional methods for calculating transport coefficients, it represents an excellent example of the use of correlation-function techniques. By splitting the total anharmonic interatomic lattice potential into its diagonal and nondiagonal contributions, $V=V_{\mathrm{d}}+V_{\mathrm{nd}}$, the effect of the equilibrium and nonequilibrium properties of the crystal lattice on the thermal conductivity can be studied separately. The current-current correlation function is calculated to second order in V in a single-phonon-lifetime approximation. While V_{nd} only contributes in this approximation to the space-time-dependent part of the correlation function, V_{d} contributes as well to the space-time-independent part. The latter contribution V_{d}^0 represents a temperature-dependent Hartree approximation of the lattice potential and determines the equilibrium properties of the crystal lattice. At constant pressure V_{d}^0 gives rise to the thermal expansion of the system, which causes a decrease of the Debye frequency with increasing temperature, resulting in a depression of the conductivity below the $1/T$ behavior. Even in the case of constant volume, the temperature dependence ot V_{d}^0 causes a decrease of the phonon frequency with increasing temperature. This again gives rise to a depression of the conductivity below the $1/T$ behavior and leads to a T^2 term in the resistivity in the region around the Debye temperature. This latter effect is studied by taking into account the entire anharmonicity of the lattice potential which leads to V_{d}^0 and calculating the space-time-dependent part of the correlation function in lowest order in the atomic displacements. Thus Peierls' expression for the conductivity is rederived in terms of the renormalized phonon frequency and group velocity due to V_{d}^0, rather than the pure harmonic approximation of the lattice potential. The entire dissipative mechanism of the system, which is given by the space-time-dependent part of the correlation function, calculated to second order in V, cancels partially the effect of V_{d}^0 on the conductivity. For temperatures around and just above the Debye temperature the temperature dependence of the lattice thermal conductivity is given by $1/T(1+\alpha T)$. With increasing temperature the conductivity reaches a minimum, which is followed by a steep rise as one approaches a dynamical instability of the system.

I. INTRODUCTION

SINCE Peierls' application of Pauli's master equation[1] to nonequilibrium properties of crystal lattices, there has been considerable interest in the question of how the perturbed distribution of the system relaxes to its equilibrium distribution. The problem of lattice thermal conductivity was then mainly the problem of finding an appropriate relaxation time. Models for relaxation processes have been studied[2] and were discussed in view of general statements one could make on the nature of Peierls' equation.[3,4]

The usual formulation of transport coefficients represents another problem in the case of the lattice thermal conductivity. In recent years the use of correlation functions for transport coefficients has been studied in great detail[5] and proved to be more general than the use of transport equations. However, the validity of such a formalism which is based on a mechanical formulation of the problem has been questioned in the case of lattice thermal conductivity. Kubo's formula[6] for the electric conductivity describing the response of the system to an external electric field can be derived by means of the exact Hamiltonian alone. In the case of lattice thermal conductivity the external disturbance is represented by a temperature gradient and so statistical properties of the system have to be taken into account. Local variables or local equilibrium have then to be assumed in order to derive a correlation function in the usual way.[7] Theoretical investigations have so far mainly been concerned with the problems of lattice thermal conductivity as outlined above.

Recently, the occurrence of anharmonic terms in the expression for the energy current was pointed out by several authors.[8] The simple-harmonic expression for the energy current (which is diagonal in the phonon variables[9] and is expressed in terms of the number of phonons, the group velocity, and phonon frequency) is corrected by diagonal and nondiagonal elements of higher order in the phonon variables. Their effect on

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[1] R. E. Peierls, Ann. Physik **3**, 1055 (1929).

[2] J. Callaway, Phys. Rev. **113**, 1046 (1959).

[3] J. A. Krumhansl and R. A. Guyer, Bull. Am. Phys. Soc. **10**, 530 (1965); J. A. Krumhansl, Proc. Phys. Soc. **85**, 921 (1965).

[4] For a detailed review of this aspect of the problem of lattice thermal conductivity see P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961).

[5] T. Matsubara, Progr. Theoret. Phys. (Kyoto) **14**, 351 (1955); P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959).

[6] R. Kubo, Can. J. Phys. **34**, 1274 (1956).

[7] J. M. Luttinger, Phys. Rev. **135**, A1505 (1964).

[8] P. Choquard, Helv. Phys. Acta **36**, 415 (1963); R. Hardy, Phys. Rev. **132**, 168 (1963); J. Ranninger, University of Vienna, Vienna, Austria, 1963 (unpublished).

[9] However, nondiagonal contributions to the energy current occur because of different polarizations. Their effect on the conductivity has been discussed in Ref. 8. Being of entirely different nature than the nondiagonal elements of the energy current pointed out above, they are negligible in the case of the static homogeneous part of the conductivity and will not be treated here.

lattice thermal conductivity has been discussed to lowest order[10] and led to the beginning of a power series in the absolute temperature. For high temperatures, where the fluctuations of the lattice atoms become very large, the higher order corrections in the energy current become very important and lead not to a diverging but rather to a very badly converging expansion for the conductivity. The usual adequate way of treating such a problem is to try to re-sum the terms of the power expansion.

Choquard has succeeded in this manner in treating the equilibrium properties of monatomic crystals in a proper way.[11] A self-consistent equation for the phonon frequencies was obtained yielding a dynamical instability of the system at a certain critical temperature T_c. A perturbation expansion of the internal energy could be re-summed and the specific heat C_v was discussed for all temperatures up to T_c.

The present paper will deal with nonequilibrium properties of lattice dynamics and in particular with the calculation of the lattice thermal conductivity. A correlation-function formalism for the conductivity is used. A consistent treatment of the perturbation expansion of the current-current correlation function enables one to sum over the time-dependent and time-independent contributions of the correlation function separately. The effect of nonequilibrium and equilibrium properties of the crystal lattice on the thermal conductivity can thus be studied independently. The equilibrium properties, as far as they play a role in transport phenomena in crystal lattices, will be briefly reviewed.

The mathematical devices developed in Ref. 11 which have proved to be particularly useful in describing equilibrium properties of lattice dynamics merit an extension to the nonequilibrium case which will be incorporated in this paper.

We will deal with the construction of an energy-current-density operator to infinite order in the atomic displacements in Sec. II of the present paper. In Sec. III, the lattice thermal conductivity will be expressed in terms of the current-current correlation function. A pair approximation will yield a closed form for the conductivity in terms of time-dependent and time-independent displacement-displacement correlations. The latter are known as the mean-square fluctuations of the lattice vibrations. An exact treatment (within the pair approximation) will be given for the time-independent part of the correlation function in Sec. IV. The resulting renormalized lattice potential and its effect on the conductivity will be studied by making a harmonic approximation for the time-dependent part of the correlation function. A formally equivalent expression to Peierls' expression for the conductivity is obtained.[12]

In Sec. V the time-dependent correlations are treated exactly (within the pair approximation) and the effect of equilibrium and nonequilibrium properties of lattice dynamics on the thermal conductivity is discussed. The temperature behavior of the thermal conductivity is given for a temperature regime from the Debye temperature up to a dynamical instability.

A correction to the lattice energy current which has the features of a diffusion current will be studied in its effect on the thermal conductivity in Sec. VI.

II. LATTICE ENERGY CURRENT

In order to treat transport phenomena in the correlation function formalism it is necessary to define the relevant quantities, i.e., energy density and energy-current density, as continuous functions in space. This, however, is not possible for crystal structure without introducing some means of continuity in such systems. As we know the correlation-function treatment is based on a phenomenological equation for the transport coefficient which gives a relation between two macroscopic quantities, the temperature gradient and the resulting energy current. Therefore, looking at the problem from a more macroscopic than microscopic point of view it seems to be more expedient not to resolve the crystal into a set of individual atoms but rather describe it as a continuum in which the crystal structure is imbedded. Hardy[8] had succeeded in formulating the energy density and energy-current density as a continuous function in space by introducing a weighting function $\Delta(\mathbf{x}-\mathbf{q}_i)$. This function measures the value of a particular quantity which is defined at lattice site $\mathbf{q}_i$ at an arbitrary point in the lattice $\mathbf{x}$. In the present paper we shall be concerned with the calculation of the homogeneous and static part of the conductivity which can be described in terms of the homogeneous part of the energy-current density alone. The device of introducing a weighting function turns out to be a good mathematical trick to evaluate the homogeneous part of the energy-current density which does not depend on the particular form of the weighting function.

Let us now define the energy density of a crystal lattice by

$$\epsilon(\mathbf{x})=\sum_i \Delta(\mathbf{x}-\mathbf{q}_i)\left[\tfrac{1}{2}\dot{q}_i^2 M+\tfrac{1}{2}\sum_{j(\neq i)} v(\mathbf{q}_j-\mathbf{q}_i)\right], \quad (1)$$

where $v(\mathbf{q}_j-\mathbf{q}_i)$ denotes the potential energy between two atoms with mass M at the lattice sites $\mathbf{q}_j$ and $\mathbf{q}_i$. Equation (1) differs from the usual expression for the crystal Hamiltonian by taking for $\Delta(\mathbf{x}-\mathbf{q}_i)$ a distribution function (e.g., Gaussian) with a finite width instead of a δ function. The definition of the total Hamiltonian

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[10] See also F. Henin and L. Blum, Bull. Classe Sci. Acad. Roy. Belg. **46**, 862 (1960).

[11] P. Choquard, *Selected Topics in Lattice Dynamics* (W. A. Benjamin, Inc., New York, to be published).

[12] A preliminary report on this topic was given at the American Physical Society Meeting, 1965 (to be published), in Washington, D. C.; J. Ranninger, Bull. Am. Phys. Soc. **10**, 504 (1965).

$H=\int d^3x\,\epsilon(\mathbf{x})$ leads to the normalization of $\Delta(\mathbf{x})$

$$\int d^3x\,\Delta(\mathbf{x})=1. \qquad (2)$$

The continuity equation

$$\partial\epsilon(\mathbf{x})/\partial t+\mathrm{div}\mathbf{J}(\mathbf{x})=0 \qquad (3)$$

will be used to derive an expression for the energy-current density $\mathbf{J}(\mathbf{x})$. Using the equation of motion

$$M\ddot{u}_i{}^\alpha(t)=-\sum_{j(\neq i)}\frac{\partial v(\mathbf{R}_{ji}+\mathbf{u}_j(t)-\mathbf{u}_i(t))}{\partial u_i{}^\alpha(t)}, \qquad (4)$$

we finally derive

$$\frac{\partial\epsilon(\mathbf{x})}{\partial t}=-\frac{\partial}{\partial x^l}\sum_i\Delta(\mathbf{x}-\mathbf{q}_i)\dot{u}_i{}^l(t)\left[\frac{\dot{u}_i{}^2(t)}{2}M+\tfrac{1}{2}\sum_{j(\neq i)}v(\mathbf{R}_{ji}+\mathbf{u}_j(t)-\mathbf{u}_i(t))\right]$$
$$-\tfrac{1}{4}\sum_{i\neq j}\{\Delta(\mathbf{x}-\mathbf{q}_j)-\Delta(\mathbf{x}-\mathbf{q}_i)\}\left[\frac{\partial v(\mathbf{R}_{ji}+\mathbf{u}_j(t)-\mathbf{u}_i(t))}{\partial u_j{}^\alpha(t)}\dot{u}_j{}^\alpha(t)-\frac{\partial v(\mathbf{R}_{ij}+\mathbf{u}_i(t)-\mathbf{u}_j(t))}{\partial u_i{}^\alpha(t)}\dot{u}_i{}^\alpha(t)\right], \qquad (5)$$

where we adopt the convention that a repeated index implies a summation.

$\mathbf{u}_i(t)$ and $\mathbf{R}_{ij}$ are defined by

$$\mathbf{u}_i(t)=\mathbf{q}_i-\mathbf{q}_i{}^0 \quad \mathbf{R}_{ij}=\mathbf{q}_i{}^0-\mathbf{q}_j{}^0=-\mathbf{R}_{ji}. \qquad (6)$$

The equilibrium position of the atom at lattice site $\mathbf{q}_i$ is denoted by $\mathbf{q}_i{}^0$. After expanding the expression in the curly bracket in (5) in powers of $\mathbf{q}_i-\mathbf{q}_j$ and using Eq. (3) we derive the energy current density

$$J^l(\mathbf{x})=\sum_i\Delta(\mathbf{x}-\mathbf{q}_i)\dot{u}_i{}^l(t)[(\tfrac{1}{2}\dot{u}_i{}^2(t))M+\tfrac{1}{2}\sum_{j(\neq i)}v(\mathbf{R}_{ji}+\mathbf{u}_j(t)-\mathbf{u}_i(t))]+\tfrac{1}{4}\sum_{i\neq j}(q_i-q_j)^l\sum_{n=0}^{\infty}\frac{1}{(n+1)!}\left[(q_i-q_j)^\alpha\frac{\partial}{\partial x^\alpha}\right]^n$$
$$\times\Delta(\mathbf{x}-\mathbf{q}_i)\left(\frac{\partial v(\mathbf{R}_{ij}+\mathbf{u}_i(t)-\mathbf{u}_j(t))}{\partial u_i{}^\beta(t)}\dot{u}_i{}^\beta(t)-\frac{\partial v(\mathbf{R}_{ji}+\mathbf{u}_i(t)-\mathbf{u}_j(t))}{\partial u_j{}^\beta(t)}\dot{u}_j{}^\beta(t)\right). \qquad (7)$$

For the calculation of the static and homogeneous part of the lattice thermal conductivity only the homogeneous part of the energy-current density plays a role. This is obtained by integrating (7) over $\mathbf{x}$ and corresponds to the Fourier transform $J^l(\mathbf{k})$ of $J^l(\mathbf{x})$ for $\mathbf{k}=0$:

$$J^l(\mathbf{k}=0)=\sum_i\dot{u}_i{}^l(t)[(\tfrac{1}{2}\dot{u}_i{}^2(t))M+\tfrac{1}{2}\sum_{j(\neq i)}v(\mathbf{R}_{ji}+\mathbf{u}_j(t)-\mathbf{u}_i(t))]+\tfrac{1}{4}\sum_{i\neq j}(q_i-q_j)^l\frac{\partial v(\mathbf{R}_{ji}+\mathbf{u}_j(t)-\mathbf{u}_i(t))}{\partial u_i{}^\alpha}(\dot{u}_j(t)+\dot{u}_i(t))^\alpha. \qquad (8)$$

The first term in (8) represents a current due to a diffusion process in our system. This term is usually of minor importance in the case of lattice thermal conductivity. However, for very high temperatures where the atomic displacements become comparable with the interatomic spacing, the effect of this diffusion term on lattice thermal conductivity has to be considered and will be discussed in Sec. VI. The second term in (8) corresponds to the proper homogeneous energy-current density in a crystal lattice. It can be written as a sum over individual energy currents $j_{\mathbf{q}_i}{}^l$ at each lattice site $\mathbf{q}_i$

$$j_{\mathbf{q}_i}{}^l=\mathbf{c}_{q_i}\cdot\textstyle\sum_j\mathbf{F}_{ij}(q_i-q_j)^l, \qquad (9)$$

where $\mathbf{c}_{q_i}$ represents the velocity of the lattice atom at site $\mathbf{q}_i$, and $\mathbf{F}_{ij}\equiv\partial v(\mathbf{R}_{ij}+\mathbf{u}_i-\mathbf{u}_j)/\partial\mathbf{u}_i$ is the force acting on the atom at $\mathbf{q}_i$ which is caused by the change of field of its surrounding atoms due to its own movement.

In the following paragraphs we will only be concerned with this part of the lattice energy current which can be written after expanding the interatomic potential in a power series of the atomic displacements $\mathbf{u}_i(t)$ as[13]

$$J^l(\mathbf{k}=0)=-\tfrac{1}{4}\sum_{i,\rho}(R_\rho+\eta_\rho u_i(t))^l\bar{\eta}_\rho\dot{\mathbf{u}}_i(t)\cdot\mathbf{p}e^{\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p}}v(R_\rho). \qquad (10)$$

Here we use for simplification of the notation,

$$\mathbf{R}_{ji}\equiv\mathbf{R}_\rho,\quad \mathbf{p}=\partial/\partial\mathbf{R}_\rho,$$
$$\eta_\rho\mathbf{u}_i(t)=(e^{\mathbf{R}_\rho\cdot(\partial/\partial\mathbf{q}_i)}-1)\mathbf{u}_i(t)=\mathbf{u}_j(t)-\mathbf{u}_i(t), \qquad (11)$$
$$\bar{\eta}_\rho\mathbf{u}_i(t)=(e^{\mathbf{R}_\rho\cdot(\partial/\partial\mathbf{q}_i)}+1)\mathbf{u}_i(t)=\mathbf{u}_j(t)+\mathbf{u}_i(t),$$

and we have to keep in mind that the operator $\mathbf{p}$ only acts on the potential $v(R_\rho)$.

The appearance of the term $(R_\rho+\eta_\rho u_i(t))^l$ rather than $R_\rho{}^l$ in expression (10) for the energy current arises from the fact that the interparticle energy is not transmitted between the lattice sites $\mathbf{q}_i{}^0$ and $\mathbf{q}_j{}^0$, but between their

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[13] From now on we will use $J^l(\mathbf{k}=0,t)$ to denote the intrinsic part of the lattice energy current alone. Later on, when we treat the diffusion current, it will be separately referred to.

actual positions at $\mathbf{q}_i$ and $\mathbf{q}_j$. For temperatures where the mean-square fluctuations of the atoms are small compared to the lattice constant the term $\eta_\rho \mathbf{u}_i(t)$ can be neglected against $\mathbf{R}_\rho$. For high temperatures where $\eta_\rho \mathbf{u}_i(t)$ becomes comparable to the size of the lattice constant, we shall see in Sec. V that the sum over ρ in (10) has to be carried out over a large range over lattice vectors $\mathbf{R}_\rho$. Then again $\mathbf{R}_\rho + \eta_\rho \mathbf{u}_i(t)$ can be approximated by $\mathbf{R}_\rho$ except for the first few lattice vectors between nearest and next-nearest neighbors.

III. CURRENT-CURRENT CORRELATION FUNCTION

In order to construct an expression for the lattice thermal conductivity we have to ask for the response of our system to an external disturbance in the form of a thermal gradient. Such a disturbance applied to our system leads to a state in which a total net flow of energy is observed. Mathematically such a state can be treated as a perturbation of another state in which the system is in equilibrium in the absence of a thermal gradient. If the external disturbance is small (which is the case in thermal conductivity measurements) a perturbation expansion to first order in the external disturbance (known as linear response) will yield a good description of the system displaying transport phenomena. If we are able by any means to construct an interaction Hamiltonian setting up an energy flow in our system it must be done in such a way that the system is never brought out of thermal equilibrium while turning on the external disturbance. This has already been pointed out by Kadanoff and Martin.[14]

The expectation value of an operator $O(\mathbf{x},t)$ in a system in thermal equilibrium is given by

$$\langle O(\mathbf{x},t)\rangle = \mathrm{Tr}\{\rho O(\mathbf{x},t)\} = \frac{\mathrm{Tr}[e^{-\beta(H-\mu N)}O(\mathbf{x},t)]}{\mathrm{Tr}e^{-\beta(H-\mu N)}}. \quad (12)$$

For a closed system, the term μN in the density matrix ρ will vanish. Let us assume that we can define a local temperature $T(\mathbf{x})$ at any arbitrary point $\mathbf{x}$ in the crystal. Changing the temperature at time t at $\mathbf{x}$ by an amount $\delta T(\mathbf{x},t)$ the density matrix can again be written in equilibrium form using the modified Hamiltonian density $\epsilon'(\mathbf{x}) = \epsilon(\mathbf{x}) + \delta\epsilon(\mathbf{x})$,

$$\delta\epsilon(\mathbf{x},t) = \epsilon(\mathbf{x},t)(\delta T(\mathbf{x},t)/T), \quad (13)$$

which arises from an expansion of $\beta(\mathbf{x},t) = KT(\mathbf{x},t)^{-1}$ in terms of $\delta T(\mathbf{x},t)$. K denotes Boltzmann's constant and T represents the uniform temperature throughout the system before the external disturbance, causing a temperature gradient, was turned on.

The familar macroscopic relation,

$$\langle J^k(\mathbf{x},t)\rangle = -2\int_{-\infty}^{t} dt' \int d^3x\, \mathcal{H}^{kl}(\mathbf{x}, \mathbf{x}', t-t') \frac{\partial}{\partial x'^l}\delta T(\mathbf{x}',t'), \quad (14)$$

will serve to define the conductivity $\mathcal{H}^{kl}(\mathbf{x},\mathbf{x}',t)$ in terms of the current-current correlation function. $J^k(\mathbf{x},t)$ in Eq. (14) denotes the energy-current density operator in the presence of the external disturbance. $\mathbf{J}(\mathbf{x},t)$ can be written in terms of the current density operator in absence of the external disturbance $\mathbf{J}_0(\mathbf{x},t)$. Taking into account only linear terms in the external disturbance we can rewrite Eq. (14) in the form

$$\langle J^k(\mathbf{x},t)\rangle = i\int_{-\infty}^{t} dt' \int d^3x' \langle [J_0{}^k(\mathbf{x},t), \epsilon(\mathbf{x}',t')]\rangle \frac{\delta T(\mathbf{x}',t')}{T}. \quad (15)$$

The expectation value of the right-hand side of (15) is to be understood as the average over initial variables of the system at time $t = -\infty$. A comparision of Eqs. (14) and (15) finally gives

$$2iT(\partial/\partial x^l)\mathcal{H}^{kl}(\mathbf{x}, \mathbf{x}', t-t') = \langle [J_0{}^k(\mathbf{x},t)\epsilon(\mathbf{x}',t')]\rangle. \quad (16)$$

Using the continuity Eq. (3) we can transform (16) into the current-current correlation function

$$\begin{aligned}\langle [J_0{}^k(\mathbf{x},t), J_0{}^l(\mathbf{x}',t')]\rangle &= \int \frac{d\omega}{\pi} \int \frac{d^3q}{(2\pi)^3} e^{i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')} e^{-i\omega(t-t')} \omega T \mathcal{H}^{kl}(\mathbf{q},\omega) \\ &= \int \frac{d\omega}{2\pi} \int \frac{d^3q}{(2\pi)^3} e^{i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')} e^{-i\omega(t-t')} \\ &\qquad \times F_>{}^{kl}(\mathbf{q},\omega)(1-e^{-\beta\omega}), \end{aligned} \quad (17)$$

and finally obtain

$$2\omega T\mathcal{H}^{kl}(\mathbf{q},\omega) = F_>{}^{kl}(\mathbf{q},\omega)(1-e^{-\beta\omega}). \quad (18)$$

$F_>{}^{kl}(\mathbf{q},\omega)$ is given by the Fourier transform of

$$F_>{}^{kl}(\mathbf{x}-\mathbf{x}', t-t') = \langle J_0{}^k(\mathbf{x},t) J_0{}^l(\mathbf{x}',t')\rangle \quad \text{for} \quad t>t'. \quad (19)$$

Analogously we define[15]

$$F_>{}^{kl}(\mathbf{x}-\mathbf{x}', t-t') = \langle J_0{}^l(\mathbf{x}',t') J_0{}^k(\mathbf{x},t)\rangle \quad \text{for} \quad t<t' \quad (20)$$

which is related to (19) by

$$F_<{}^{kl}(\mathbf{x}-\mathbf{x}', \omega) = e^{-\beta\omega} F_>{}^{kl}(\mathbf{x}-\mathbf{x}', \omega). \quad (21)$$

The causal two-point function $F^{kl}(\mathbf{x}-\mathbf{x}', t-t')$ is then given in terms of $F_>{}^{kl}(\mathbf{x}-\mathbf{x}', t-t')$ and $F_<{}^{kl}(\mathbf{x}-\mathbf{x}', t-t')$ by[16]

$$\begin{aligned} F^{kl}(\mathbf{x}-\mathbf{x}', t-t') &\equiv \langle T\{J_0{}^k(\mathbf{x},t) J_0{}^l(\mathbf{x}',t')\}\rangle \\ &= F_<{}^{kl}(\mathbf{x}-\mathbf{x}', t-t')\theta(t'-t) \\ &\quad + F_>{}^{kl}(\mathbf{x}-\mathbf{x}', t-t')\theta(t-t'). \end{aligned} \quad (22)$$

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[14] L. P. Kadanoff and P. C. Martin, Phys. Rev. **124**, 670 (1961).

[15] K. Baumann and J. Ranninger, Ann. Phys. (N. Y.) **20**, 157 (1962).

[16] Here we have to take the expectation value of the time-ordered product of the energy currents which is denoted by $T\{J^k(\mathbf{x}t)J^l(\mathbf{x}'t')\}$. Since in the following calculation of the conductivity we always will deal with causal Green's functions, we shall omit the symbol T in front of the operators from now on and understand under each expectation value of two operators as the expectation value of their time-ordered product.

After expressing Eq. (18) in terms of the causal Green's function $F^{kl}(\mathbf{x}-\mathbf{x}', t-t')$, we obtain a Kubo formula for the lattice thermal conductivity

$$\mathrm{Re}F^{kl}(\mathbf{q}=0, \omega\rightarrow 0)=-2KT^2\mathcal{K}^{kl}(\mathbf{q}=0, \omega\rightarrow 0)\,. \quad (23)$$

Inserting expression (10) for the homogeneous part of the lattice energy current into (22) the current-current correlation function can be expressed in terms of the atomic-displacement operators

$$F^{kl}(\mathbf{q}=0, \omega\rightarrow 0)$$
$$=\frac{1}{16}\int_{-\infty}^{\infty} d(t-t') \sum_{ij\rho\rho'} \langle (R_\rho+\eta_\rho u_i(t))^k \bar{\eta}_\rho \dot{\mathbf{u}}_i(t)\cdot\mathbf{p}e^{\eta_\rho \mathbf{u}_i(t)\cdot\mathbf{p}}$$
$$\times (R_{\rho'}+\eta_{\rho'}u_j(t'))^l \bar{\eta}_{\rho'}\dot{\mathbf{u}}_j(t')\cdot\mathbf{p}' e^{\eta_{\rho'}\mathbf{u}_j(t')\cdot\mathbf{p}'}\rangle v(R_\rho)v(R_{\rho'})\,. \quad (24)$$

The matrix element in (24) will now be calculated in the pair approximation. This means expressing it as a product of all possible contractions of operators in (24). In other words we shall approximate the n-particle Green's function in (24) by a product of one-particle Green's functions. This will finally lead to the appearance of the single-phonon lifetime rather than the relaxation time in the expression for the conductivity. In order to obtain the relaxation time in the conductivity we would have to write the n-particle Green's function in terms of a product of a one-particle Green's function plus a product of one-particle with two-particle Green's functions and so on. The procedure of obtaining the exact current-current correlation function is clear; however, to calculate it one step beyond our approximation is already extremely difficult. In Fig. 1 a Feynmann diagram representation for the exact current-current correlation function and its pair approximation is given.

As pointed out above, the term $\mathbf{R}_\rho+\eta_\rho\mathbf{u}_i(t)$ in the expression for the energy current can be approximated by $\mathbf{R}_\rho$. Here we shall now calculate the current-current correlation function by replacing $\mathbf{R}_\rho+\eta_\rho\mathbf{u}_i$ by $\mathbf{R}_\rho$. The contribution to the correlation function left out by this replacement will be discussed together with the diffusive part of the correlation function in VI.

In this way we obtain for the current-current correlation function

$$F^{kl}(\mathbf{q}=0, \omega\rightarrow 0)$$
$$=\frac{1}{16}\int_{-\infty}^{\infty} d(t-t') \sum_{ij\rho\rho'} R_\rho{}^k R_{\rho'}{}^l \langle \bar{\eta}_\rho \dot{\mathbf{u}}_i(t)\cdot\mathbf{p}e^{\eta_\rho \mathbf{u}_i(t)\cdot\mathbf{p}}$$
$$\times \bar{\eta}_{\rho'}\dot{\mathbf{u}}_j(t')\cdot\mathbf{p}' e^{\eta_{\rho'}\mathbf{u}_j(t')\cdot\mathbf{p}'}\rangle v(R_\rho)v(R_{\rho'})\,, \quad (25)$$

which contains now the effect of the entire anharmonicity of the interatomic potential. In order to calculate the matrix element in (25) let us consider the typical term

$$\bar{\eta}_\rho\dot{\mathbf{u}}_i(t)\cdot\mathbf{p}(1/n!)(\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p})^n$$
$$\times\bar{\eta}_{\rho'}\dot{\mathbf{u}}_j(t')\cdot\mathbf{p}'(1/n'!)(\eta_{\rho'}\mathbf{u}_j(t')\cdot\mathbf{p}')^{n'}\,, \quad (26)$$

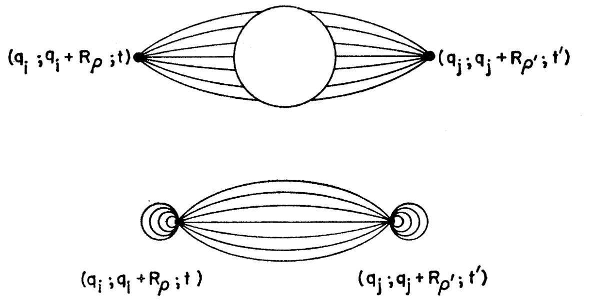

FIG. 1. Diagramatic representation of the current-current correlation function and its pair approximation. The circle represents the total vertex for n-phonon processes.

from which we have to take all possible contractions. Contractions of two different types can be made in (26), those corresponding to operators belonging to the same time and those belonging to different times. Contractions of the first type lead us to consider the term

$$\bar{\eta}_\rho\dot{\mathbf{u}}_i(t)\cdot\mathbf{p}(1/n!)(\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p})^n \quad (27)$$

by itself. Since $2r$ is an integer between 0 and the largest even integer below or equal to n, the term $(\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p})^{2r}$ can be contracted in $(2r-1)!!=(2r)!/r!2^r$ ways and we obtain

$$\langle(\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p})^{2r}\rangle=((2r)!/r!)(\tfrac{1}{2}\langle(\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p})^2\rangle)^r\,.$$

Taking into account that we have

$$\binom{n}{2r}$$

possible ways of choosing a combination of $2r$ elements $(\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p})$ out of a set of n, the contraction of (27), can be written

$$\bar{\eta}_\rho\dot{\mathbf{u}}_i(t)\cdot\mathbf{p}\frac{(\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p})^{n-2r}}{(n-2r)!}\frac{1}{r!}(\tfrac{1}{2}\langle(\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p})^2\rangle)^r\,. \quad (28)$$

Contractions of the form $\langle\bar{\eta}_\rho\dot{\mathbf{u}}_i(t)\cdot\mathbf{p}\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p}\rangle$ contain the Fourier transform of $\bar{\eta}_\rho\eta_{-\rho}$, which is an odd function of the phonon momenta, and vanish therefore.

Having done all the contractions of the first type in (26) we have to consider now

$$(\bar{\eta}_\rho\dot{\mathbf{u}}_i(t)\cdot\mathbf{p})[(n-2r)!]^{-1}(\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p})^{n-2r}(\bar{\eta}_{\rho'}\dot{\mathbf{u}}_j(t')\cdot\mathbf{p}')$$
$$\times[(n'-2r')!]^{-1}(\eta_{\rho'}\mathbf{u}_j(t')\cdot\mathbf{p}')^{n'-2r'}(r!)^{-1}(\tfrac{1}{2}\langle(\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p})^2\rangle)^r$$
$$\times(r'!)^{-1}(\tfrac{1}{2}\langle(\eta_{\rho'}\mathbf{u}_j(t')\cdot\mathbf{p}')^2\rangle)^{r'}\,. \quad (29)$$

In the pair approximation, $n-2r$ has to be equal to $n'-2r'\equiv a$. After doing a similar combinatoric exercise as carried out above for the contractions of the first type, for the contractions of the second kind in (29), we obtain

$$[\langle(\bar{\eta}_\rho\dot{\mathbf{u}}_i(t)\cdot\mathbf{p})(\bar{\eta}_{\rho'}\dot{\mathbf{u}}_j(t')\cdot\mathbf{p}')\rangle+\langle(\bar{\eta}_\rho\dot{\mathbf{u}}_i(t)\cdot\mathbf{p})(\eta_{\rho'}\mathbf{u}_j(t')\cdot\mathbf{p}')\rangle$$
$$\times\langle(\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p})(\bar{\eta}_\rho\dot{\mathbf{u}}_j(t')\cdot\mathbf{p}')\rangle]$$
$$\times(a!)^{-1}(\langle\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p}\eta_{\rho'}\mathbf{u}_j(t')\cdot\mathbf{p}'\rangle)^a$$
$$\times(r!)^{-1}(\tfrac{1}{2}\langle(\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p})^2\rangle)^r(r'!)^{-1}(\tfrac{1}{2}\langle(\eta_{\rho'}\mathbf{u}_j(t')\cdot\mathbf{p}')^2\rangle)^{r'}\,. \quad (30)$$

After carrying out the summations over r, r' and a we can write the current-current correlation function in the pair approximation $F_p{}^{kl}(\mathbf{q}=0,\omega\rightarrow 0)$ as

$$\begin{aligned}F_p{}^{kl}&(\mathbf{q}=0,\omega\rightarrow 0)\\&=\frac{1}{16}\int_{-\infty}^{\infty}d(t-t')\sum_{ij\rho\rho'}R_\rho{}^k R_{\rho'}{}^l[\langle\bar{\eta}_\rho\dot{\mathbf{u}}_i(t)\cdot\mathbf{p}\bar{\eta}_{\rho'}\dot{\mathbf{u}}_j(t')\cdot\mathbf{p}'\rangle\\&\quad+\langle\bar{\eta}_\rho\dot{\mathbf{u}}_i(t)\cdot\mathbf{p}\eta_{\rho'}\mathbf{u}_j(t')\cdot\mathbf{p}'\rangle\langle\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p}\bar{\eta}_{\rho'}\dot{\mathbf{u}}_j(t')\cdot\mathbf{p}'\rangle]\\&\quad\times\exp[\tfrac{1}{2}\langle(\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p}+\eta_{\rho'}\mathbf{u}_j(t')\cdot\mathbf{p}')^2\rangle]v(R_\rho)v(R_{\rho'}).\end{aligned}\tag{31}$$

IV. THE QUASIHARMONIC CRYSTAL

The anharmonic terms in the lattice potential contribute to the current-current correlation function in essentially two different ways. The first in terms of the total contribution of the contractions of the first kind, the second in terms of the total contribution of the contractions of the second kind. Contractions of the first and second kind occur in the current-current correlation function factorized

$$\begin{aligned}\exp[\tfrac{1}{2}\langle(\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p}+\eta_{\rho'}\mathbf{u}_j(t')\cdot\mathbf{p}')^2\rangle]\\=\exp[\tfrac{1}{2}\lambda_\rho pp+\lambda_{\rho\rho'}{}^{ij}(t'-t)pp'+\tfrac{1}{2}\lambda_{\rho'}p'p']\end{aligned}$$

where the matrix

$$\lambda^{\alpha\beta}=\langle\eta_\rho\eta_\rho u_i{}^\alpha(t)u_j{}^\beta(t)\rangle\tag{32}$$

denotes the contractions of the first kind and

$$\lambda_{\rho\rho'}{}^{ij}(t-t')^{\alpha\beta}=\langle\eta_\rho\eta_{\rho'}u_i{}^\alpha(t)u_j{}^\beta(t')\rangle\tag{33}$$

the contractions of the second kind. The above expressions $\lambda_\rho pp$, respectively $\lambda_{\rho\rho'}{}^{ij}(t-t')pp'$ are to be understood as the matrix products $\lambda_\rho{}^{\alpha\beta}p^\alpha p^\beta$, respectively, $\lambda_{\rho\rho'}{}^{ij}(t-t')^{\alpha\beta}p^\alpha p'^\beta$.

The particular way in which the anharmonic terms of the interatomic potential enter the correlation function (31) enables us to study the physical meaning of λ_ρ and $\lambda_{\rho\rho'}{}^{ij}(t-t')$ on the thermal conductivity in a systematic way. Starting out with the lowest order approximation to (31)[17]

$$\begin{aligned}F_{p,h}{}^{kl}(\mathbf{q}=0,\omega\rightarrow 0)&=\frac{1}{16}\int_{-\infty}^{+\infty}d(t-t')\sum_{ij\rho\rho'}R_\rho{}^k R_{\rho'}{}^l\{\langle\bar{\eta}_\rho\dot{\mathbf{u}}_i(t)\cdot\mathbf{p}\bar{\eta}_{\rho'}\dot{\mathbf{u}}_j(t')\cdot\mathbf{p}'\rangle\\&\quad\times\langle\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p}\eta_{\rho'}\mathbf{u}_j(t')\cdot\mathbf{p}'\rangle+\langle\bar{\eta}_\rho\dot{\mathbf{u}}_i(t)\cdot\mathbf{p}\eta_{\rho'}\mathbf{u}_j(t')\cdot\mathbf{p}'\rangle\langle\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p}\bar{\eta}_{\rho'}\dot{\mathbf{u}}_j(t')\cdot\mathbf{p}'\rangle\}v(R_\rho)v(R_{\rho'})\\&=\frac{1}{16}\int_{-\infty}^{+\infty}d(t-t')\sum_{ij\rho\rho'}R_\rho{}^k R_{\rho'}{}^l\langle\bar{\eta}_\rho\dot{\mathbf{u}}_i(t)\cdot\mathbf{p}\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p}\bar{\eta}_{\rho'}\dot{\mathbf{u}}_j(t')\cdot\mathbf{p}'\eta_{\rho'}\mathbf{u}_j(t')\cdot\mathbf{p}'\rangle v(R_\rho)v(R_{\rho'})\end{aligned}\tag{34}$$

we see from the last part of Eq. (32) that this approximation corresponds to the energy current in a harmonic lattice

$$J_{0,h}{}^l(\mathbf{q}=0,t)=-\tfrac{1}{4}\sum_{i\rho}R_\rho{}^l\bar{\eta}_\rho\dot{\mathbf{u}}_i(t)\cdot\mathbf{p}\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p}v(R_\rho).\tag{35}$$

The harmonic approximation to the current-current correlation function (32) has been treated in great detail[8] and led to Peierls' result for the lattice thermal conductivity.

The immediate next step for the systematical investigation of (31) is to include now the total contributions of the contractions of the first kind on top of the harmonic approximation (32). We thus obtain

$$\begin{aligned}F_{p,qh}{}^{kl}(\mathbf{q}=0,\omega\rightarrow 0)&=\frac{1}{16}\int_{-\infty}^{\infty}d(t-t')\sum_{ij\rho\rho'}R_\rho{}^k R_{\rho'}{}^l\\&\quad\times\langle\bar{\eta}_\rho\dot{\mathbf{u}}_i(t)\cdot\mathbf{p}\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p}\bar{\eta}_{\rho'}\dot{\mathbf{u}}_j(t')\cdot\mathbf{p}'\eta_{\rho'}\mathbf{u}_j(t')\cdot\mathbf{p}'\rangle\\&\quad\times e^{\frac{1}{2}\lambda_\rho pp}v(R_\rho)e^{\frac{1}{2}\lambda_{\rho'}p'p'}v(R_{\rho'})\end{aligned}\tag{36}$$

and the corresponding energy current operator reads

$$\begin{aligned}J_{0,qh}{}^l(\mathbf{q}=0,t)=-\tfrac{1}{4}\sum R_\rho{}^l\bar{\eta}_\rho\dot{\mathbf{u}}_i(t)\cdot\mathbf{p}\\\times\eta_\rho\mathbf{u}_j(t)\cdot\mathbf{p}e^{\frac{1}{2}\lambda_\rho pp}v(R_\rho).\end{aligned}\tag{37}$$

The similarity between (37) and (35) is obvious and we see that $J_{0,qh}{}^l$ corresponds to an energy current in a harmonic crystal with the modified interatomic potential

$$V(R_\rho)=e^{\frac{1}{2}\lambda_\rho pp}v(R_\rho).\tag{38}$$

$J_{0,qh}{}^l$ will, therefore, be referred to as the quasiharmonic energy current and the potential $V(R_\rho)$ will be called quasiharmonic potential.

From the analogy of the quasiharmonic energy current to the harmonic one we anticipate that $J_{0,qh}{}^l$ again can be written in the phenomenological way in terms of the group velocity, the phonon energy, and the number of phonons. In order to express $J_{0,qh}{}^l$ in these quantities let us first take a closer look at the equation of motion

$$M\ddot{u}_i{}^\alpha=(e^{\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p}}-1)p^\alpha v(R_\rho).\tag{39}$$

The approximation to the current-current correlation function we choose, namely the pair approximation (31), describes the dissipative properties of the system in terms of the single-phonon lifetime. Two-particle and higher order Green's functions which would lead to a description of the thermal conductivity in terms of a relaxation time are not taken into account. The dissipa-

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[17] The first term in an expansion of the exponent in (31) is proportional to the stress tensor $R_\rho{}^l p^k v(R_\rho)$. In order to fulfill the stability conditions, the components of the stress tensor are required to be zero, see M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1956), p. 132.

tion mechanism resulting from such an approximation is described by the linearized master equation which is obtained by linearizing the equation of motion. In order to carry out the appropriate procedure for the linearization of (37) and to find its corresponding solutions let us discuss the equation of motion in terms of the single-phonon Green's function $\langle \mathbf{u}_i(t)\mathbf{u}_j(t')\rangle$. Multiplying (37) by $u_j^\alpha(t')$ and taking the expectation value of the time-ordered product, we obtain

$$M\langle \ddot{u}_i^\alpha(t)u_j^\alpha(t')\rangle=\langle(e^{\eta_\rho \mathbf{u}_i(t)\cdot\mathbf{p}}-1)u_j^\alpha(t')\rangle p^\alpha v(R_\rho)\,. \qquad (40)$$

Before proceeding to an examination of (40) let us go over to the phonon variables. The most general way of describing a lattice wave, characterized by the atomic displacements in a crystal lattice is in the form of the Fourier superposition of plane waves

$$u_i^\alpha(t)=\frac{1}{MN}\sum_{\mathbf{k}p} e_{\mathbf{k}p}{}^\alpha\frac{a_{\mathbf{k}p}(t)+a_{-\mathbf{k}p}{}^\dagger(t)}{(2\omega_{\mathbf{k}p})^{1/2}}e^{i\mathbf{k}\cdot\mathbf{q}_i}\,. \qquad (41)$$

The number of lattice sites is denoted by N. The phonon creation and annihilation operators $a_{\mathbf{k}p}{}^\dagger(t)$ and $a_{\mathbf{k}p}(t)$ fulfill the usual Bose commutation relations

$$\begin{aligned}[][a_{\mathbf{k}p}(t),a_{\mathbf{k}'p'}(t)]&=[a_{\mathbf{k}p}{}^\dagger(t),a_{\mathbf{k}'p'}{}^\dagger(t)]=0\,,\\ [a_{\mathbf{k}p}(t),a_{\mathbf{k}'p'}{}^\dagger(t)]&=\delta_{pp'}\delta_{\mathbf{k},\mathbf{k}'+\mathbf{K}}\,,\end{aligned} \qquad (42)$$

where $\mathbf{K}$ can be any reciprocal lattice vector and where we work in units $\hbar=1$. The polarization vectors $e_{\mathbf{k}p}=e_{-\mathbf{k}p}{}^\dagger$ obey the orthonormality and completeness relations

$$\textstyle\sum_\alpha e_{\mathbf{k}p}{}^{\alpha\dagger}e_{\mathbf{k}p'}{}^\alpha=\delta_{pp'}\,,\quad \sum_{\mathbf{k}} e_{\mathbf{k}p}{}^{\alpha\dagger}e_{\mathbf{k}p}{}^\beta=\delta^{\alpha\beta}\,. \qquad (43)$$

In the lowest order perturbation theory we can write Eq. (40) in terms of the harmonic expectation values

$$\begin{aligned}\textstyle\sum_\alpha M\langle\ddot{u}_i^\alpha(t)u_j^\alpha(t')\rangle_h&\\ =\langle\eta_\rho\mathbf{u}_i(t)\cdot\mathbf{p}\mathbf{u}_j(t')\cdot\mathbf{p}\rangle_h &\exp(\tfrac{1}{2}{}^h\lambda_\rho pp)v(R_\rho)\,,\end{aligned} \qquad (44)$$

where ${}^h\lambda_\rho$ indicates that the harmonic expectation values has to be taken in (32). A common factor of both sides of Eq. (44), namely $\langle u_i^\alpha(t)u_j^\alpha(t')\rangle_h$ can be canceled after expressing (44) in terms of the phonon variables and we obtain the equation for the phonon frequency

$$\begin{aligned}\omega_{\mathbf{k}p}{}^2\delta_{pp'}=M^{-1}\tfrac{1}{2}&\textstyle\sum_\rho \eta_\rho{}^{\mathbf{k}}\eta_\rho{}^{-\mathbf{k}}\\ &\times e_{\mathbf{k}p}{}^\alpha e_{\mathbf{k}p'}{}^{\beta\dagger}p^\alpha p^\beta\exp(\tfrac{1}{2}{}^h\lambda_\rho pp)v(R_\rho)\,.\end{aligned} \qquad (45)$$

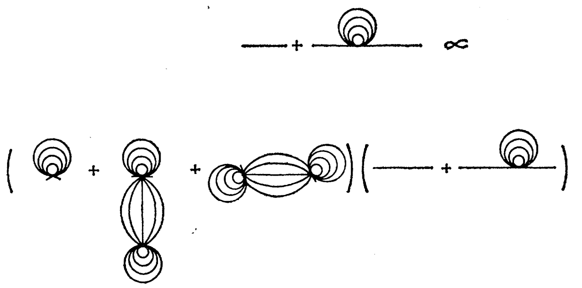

FIG. 2. Diagramatic representation of the equation of motion in second-order perturbation theory in the anharmonic interatomic lattice potential.

The Fourier transforms of η_ρ and $\bar{\eta}_\rho$ are denoted by

$$\eta_\rho{}^{\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{R}_\rho}-1 \quad\text{and}\quad \bar{\eta}_\rho{}^{\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{R}_\rho}+1\,.$$

From the right-hand side of expression (45) we see that we obtain this first-order linearization of the equation of motion by taking the Hartree approximation of the interatomic potential. This corresponds to a real contribution to the phonon self-energy. In order to obtain a complex self-energy describing a single-phonon lifetime, (40) has therefore to be evaluated to higher order in the interatomic potential. A cancellation of common factors is again possible if we evaluate the left-hand side of (40) to second order and the right-hand side to third order in the anharmonic lattice potential. A diagramatic representation corresponding to this approximation is given in Fig. 2 where the cancellation of common factors is made obvious. Analytically we obtain the following expression for this approximation after having cancelled the common factors

$$\begin{aligned}M\omega_{\mathbf{k}p}{}^2=\tfrac{1}{2}\sum_\rho \eta_\rho{}^{\mathbf{k}}\eta_\rho{}^{-\mathbf{k}}e_{\mathbf{k}p}{}^\alpha e_{\mathbf{k}p}{}^{\beta\dagger}p^\alpha p^\beta\exp(\tfrac{1}{2}{}^h\lambda_\rho pp)v(R_\rho)+\tfrac{1}{2}\sum_{\mathbf{Q}\rho\rho'}\int_{-\infty}^{\infty}d\tau\exp(\tfrac{1}{2}{}^h\lambda_\rho pp)(\exp[{}^h\lambda_{\rho\rho'}{}^{\mathbf{Q}}(\tau)pp']-1-{}^h\lambda_{\rho\rho'}{}^{\mathbf{Q}}(\tau)pp')&\\ \times\exp(\tfrac{1}{2}{}^h\lambda_{\rho'}p'p')[\eta_\rho{}^{\mathbf{k}}\eta_\rho{}^{-\mathbf{k}}e_{\mathbf{k}p}{}^\alpha e_{\mathbf{k}p}{}^{\beta\dagger}p^\alpha p^\beta+\eta_\rho{}^{\mathbf{k}}\eta_{\rho'}{}^{-\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{Q}}\cos(\omega_{\mathbf{k}p}{}^h\tau)e_{\mathbf{k}p}{}^\alpha e_{\mathbf{k}p}{}^{\beta\dagger}p^\alpha p'^\beta]v(R_\rho)v(R_{\rho'})\,,&\end{aligned} \qquad (46)$$

where $\omega_{\mathbf{k}p}{}^h$ denotes the harmonic-phonon frequency. The superscript h on λ_ρ and $\lambda_{\rho\rho'}{}^{\mathbf{Q}}(\tau)$ reminds us that we have to take the harmonic expectation value in (32) and (33). From a comparison of (46) with (45) we see that our second-order corrections to (40) contributed in two physically distinct ways. The second term in (46) corresponds to a higher order Hartree approximation for the phonon self-energy and thus yields a correction to the phonon frequency. The last term in (46) however represents the lowest order term in the complex phonon self-energy and thus yields the desired single-phonon lifetime. Because of the physical distinction between the different contributions of the phonon self-energy in (46) and their difference in order of magnitude, an independent examination of the real and imaginary parts of (46) is justified. The equation for the phonon frequency, given now entirely by the real part of Eq. (46) will be treated in a self-consistent way. The phonon frequency $\hat{\omega}_{\mathbf{k}p}$ thus obtained will then replace $\omega_{\mathbf{k}p}{}^h$ in the imaginary part of (43). Such a procedure corresponds to a self-consistent treatment of Eq. (43) where we consider the imaginary part of the phonon self-energy as a small perturbation correction to the total phonon self-energy. In other words we treat (46) to all orders in the real part of the self-energy and deal with the imaginary part in first-order perturbation theory.

Writing the total phonon self-energy $\omega_{\mathbf{k}p}$ as $\omega_{\mathbf{k}p}=\mathrm{Re}\,\omega_{\mathbf{k}p}+i\,\mathrm{Im}\,\omega_{\mathbf{k}p}$, the following expression for $\mathrm{Im}\,\omega_{\mathbf{k}p}$ is obtained,

$$\begin{aligned}\mathrm{Im}\,\omega_{\mathbf{k}p}=\mathrm{Im}\frac{1}{2\hat{\omega}_{\mathbf{k}p}}\sum_{\mathbf{Q}\rho\rho'}\int_{-\infty}^{\infty}d\tau\,\exp(\tfrac{1}{2}\hat{\lambda}_\rho pp)\\ \times(\exp[\hat{\lambda}_{\rho\rho'}{}^{\mathbf{Q}}(\tau)pp']-1-\hat{\lambda}_{\rho\rho'}{}^{\mathbf{Q}}(\tau)pp')\\ \times\exp(\tfrac{1}{2}\hat{\lambda}_{\rho'}p'p')\eta_\rho{}^{\mathbf{k}}\eta_{\rho'}{}^{-\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{Q}}\cos(\hat{\omega}_{\mathbf{k}p}\tau)\\ \times e_{\mathbf{k}p}{}^{\alpha}e_{\mathbf{k}p}{}^{\beta\dagger}p^{\alpha}p'^{\beta}v(R_\rho)v(R_{\rho'})\,.\end{aligned}\tag{47}$$

Here we already substituted $\hat{\omega}_{\mathbf{k}p}$ for $\mathrm{Re}\,\omega_{\mathbf{k}p}$ and the caret on λ_ρ and $\lambda_{\rho\rho'}{}^{\mathbf{Q}}(\tau)$ reminds us that the appropriate expectation value which has to be taken in (32) and (33) is the one corresponding to a crystal Hamiltonian with the eigenfrequencies $\hat{\omega}_{\mathbf{k}p}$.

Before going over to a phenomenological formulation of the energy current let us discuss the self-consistent equation for the phonon frequency.

A. Equation of Motion in a Quasiharmonic Crystal

In order to examine the self-consistent equation for the phonon frequency it is convenient to express λ_ρ and $\lambda_{\rho\rho'}{}^{\mathbf{Q}}(\tau)$ in terms of the phonon variables. Using the relations (41) and (43) we obtain

$$\begin{aligned}\lambda_\rho&=\tfrac{1}{2}\sum_{\mathbf{k}p}\eta_\rho{}^{\mathbf{k}}\eta_\rho{}^{-\mathbf{k}}(\omega_{\mathbf{k}p})^{-1}(n(\omega_{\mathbf{k}p})+\tfrac{1}{2})e_{\mathbf{k}p}{}^{\alpha}e_{\mathbf{k}p}{}^{\beta\dagger}\,,\\ \lambda_{\rho\rho'}{}^{\mathbf{Q}}(\tau)&=\tfrac{1}{2}\sum_{\mathbf{k}p}\eta_\rho{}^{\mathbf{k}}\eta_{\rho'}{}^{-\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{Q}}(2\omega_{\mathbf{k}p})^{-1}\\ &\quad\times[G(\mathbf{k},p;\,\tau)+G(-\mathbf{k},\,p;\,-\tau)]e_{\mathbf{k}p}{}^{\alpha}e_{\mathbf{k}p}{}^{\beta\dagger}.\end{aligned}\tag{48}$$

The propagator for a phonon with wave vector $\mathbf{k}$ and polarization p is defined by

$$\begin{aligned}iG(\mathbf{k},p;\,\tau)\delta_{\mathbf{k},\mathbf{k}'+\mathbf{K}}&=\langle a_{\mathbf{k}p}{}^{(0)}a_{\mathbf{k}'p}{}^{\dagger}(\tau)\rangle\\ &=\int_{-\infty}^{\infty}\frac{d\epsilon}{2\pi}e^{i\epsilon\tau}\int\frac{d\omega}{2\pi}\frac{1}{\omega-\epsilon+i\delta}\frac{1}{e^{-\beta\omega}-1}\\ &\quad+\frac{1}{\omega-\epsilon-i\delta}\frac{1}{e^{\beta\omega}-1}A(\mathbf{k},p;\,\omega)\,.\end{aligned}\tag{49}$$

The spectral function of the one-particle Green's function is given by

$$A(\mathbf{k},p;\,\omega)=\frac{\Gamma(\mathbf{k},p;\omega)}{(\omega-\mathrm{Re}\,\Sigma(\mathbf{k},p;\,\omega))^2+[\Gamma(\mathbf{k},p;\,\omega)/2]^2}\,.\tag{50}$$

$\Gamma(\mathbf{k},p;\,\omega)$ denotes the spectral function of the phonon self-energy $\Sigma(\mathbf{k},p;\,\omega)$ and differs from the expression for the single phonon lifetime [given by $\mathrm{Im}\,\Sigma(\mathbf{k},p;\,\omega)$] by a factor $\coth(\tfrac{1}{2}\beta\omega)$.

In this paper we are primarily interested in the temperature region where the anharmonic terms in the lattice potential can be expected to become important in the calculation of transport phenomena in crystal lattices. This will be the temperature regime from the Debye temperature upwards. In this case λ_ρ can be written as

$$\lambda_\rho=\tfrac{1}{2}KT\sum_{\mathbf{k}p}\eta_\rho{}^{\mathbf{k}}\eta_\rho{}^{-\mathbf{k}}\omega_{\mathbf{k}p}{}^{-2}e_{\mathbf{k}p}{}^{\alpha}e_{\mathbf{k}p}{}^{\beta\dagger}.\tag{51}$$

The lowest order self-consistent equation for the phonon frequencies is obtained from (45) by replacing $\omega_{\mathbf{k}p}{}^{h}$ by $\omega_{\mathbf{k}p}$. A multiplication of Eq. (45) by $KT/\omega_{\mathbf{k}p}{}^2$ and a subsequent summation over all wave vectors $\mathbf{k}$ and polarizations p yields in the high-temperature limit.

$$KT=\tfrac{1}{2}\textstyle\sum_\rho\lambda_\rho ppe^{\frac{1}{2}\lambda_\rho pp}v(R_\rho)\,.\tag{52}$$

As we can see from the expression (36) for the current-current correlation function and from the self-consistent equation (52), it is more convenient to use λ_ρ and $\lambda_{\rho\rho'}{}^{\mathbf{Q}}(\tau)$ instead of the absolute temperature T as natural variables in our problem. The lattice thermal conductivity will be studied as a function of these variables and its final conversion to an expression in the absolute temperature will be made by using Eq. (52) to express λ_ρ as a function of T.

The self-consistent Eq. (52) is discussed in great detail in Ref. 11 for the case where the volume of the system is kept constant. The following model for the interatomic potential was there used

$$v(R_\rho)=d_1e^{-R_\rho{}^2/c_1{}^2}-d_2e^{-R_\rho{}^2/c_2{}^2}\,,\tag{53}$$

where the parameters d_1, d_2, $c_1{}^2$, and $c_2{}^2$ can be fitted to a realistic lattice potential.

Near the Debye temperature we obtain the expected linear dependence of λ_ρ. Increasing the temperature in (52), a certain critical value T_c is reached so that for any T larger than T_c there exists no real solution λ_ρ to the self-consistent equation of motion (52). The temperature dependance for λ_ρ in this region is given by

$$\lambda_\rho=\lambda_{\rho c}-A(T_c-T)^{1/2}\,,\tag{54}$$

where A is a constant. $\lambda_{\rho c}$ refers to the maximum value of the mean square fluctuation λ_ρ up to which the system remains dynamically stable. Detailed examination of (52) shows that the repulsive part of the interatomic potential (53) plays the dominant role and leads to the occurrence of the dynamical instability by keeping the lattice constant fixed. The attractive part of (53) taken into account causes only a slight shift of λ_c and does not change the qualitative picture of the dynamical properties of lattice dynamics. Even replacing the soft part of the repulsive part of the potential (53) by a hard core does not influence the occurrence of the dynamical instability. A second root of (52) appears describing a cellular mode of our system. This, however, occurs for mean square fluctuations much larger than λ_c. For a

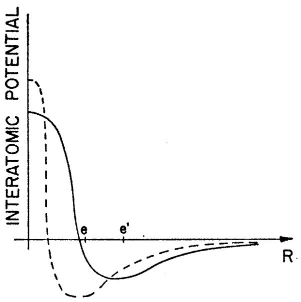

FIG. 3. The harmonic (dashed curve) and the smeared quasiharmonic interatomic potential (solid curve) as a function of the interatomic spacing R. The shift of the lattice constant from e to e' is indicated.

detailed examination of these effects the reader is referred to Ref. 11.

In this paper we are dealing only with the solid-state phase of crystal lattices and thus for the above-mentioned reasons the model potential (53) will serve to lead to a proper discription of the conductivity for high temperature below T_c.

Second-order corrections to the Hartree approximation of the interatomic potential do not change the qualitative picture of the physical properties of our system.[11] For this reason we shall treat the real part of Eq. (46) in first order in the interatomic potential and use second-order perturbation theory only for the purpose of establishing an expression for the single-phonon lifetime (47).

Consequently, the carats on $\omega_{\mathbf{k}p}$ and λ_ρ in the expression for the single-phonon lifetime have then to be replaced by bars on the same quantities. $\bar{\omega}_{\mathbf{k}p}$ will denote the solution of the self-consistent form of Eq. (45) and $\bar{\lambda}_\rho$ reminds us that we have to insert $\bar{\omega}_{\mathbf{k}p}$ for $\omega_{\mathbf{k}p}$ in (48).

Now what is the physical meaning of the potential $V(R_\rho)$ which contains already a whole subseries of anharmonic terms of the lattice potential? As pointed out above $V(R_\rho)$ corresponds to a Hartree approximation of the interatomic potential. In other words, it describes the average effect of the fluctuating lattice atoms around their equilibrium position in terms of the bare potential $v(R_\rho)$, which can be looked upon as describing the interatomic potential of a rigid lattice. Once the lattice atoms start to wiggle around their equilibrium positions they will create an effective potential which is given in lowest order perturbation theory by $V(R_\rho)$.

Using the simple model potential for $v(R_\rho)$ given in (53), we obtain

$$V(R_\rho)=d_1\left(\frac{c_1^2}{c_1^2+4\lambda_\rho}\right)^{3/2}e^{-R_\rho^2/(c_1^2+4\lambda_\rho)}-d_2\left(\frac{c_2^2}{c_2^2+4\lambda_\rho}\right)^{3/2}e^{-R_\rho^2/(c_2^2+4\lambda_\rho)}. \quad (55)$$

With increasing temperature λ_ρ in (55) increases and causes a smearing and a shift of the minimum of the potential. A comparative illustration of $v(R_\rho)$ and $V(R_\rho)$ is given in Fig. 3. In the case of constant pressure the minimum of the potential corresponds to the equilibrium position of the nearest-neighbor lattice site and thus is directly a measure for the lattice constant. In this way the thermal expansion of the system is described by $V(R_\rho)$.

Consequently, the second step in this investigation of the current-current correlation function (36) will deal with the effect of thermal expansion on the lattice thermal conductivity.

B. Energy Current in a Quasiharmonic Crystal and the Corresponding Conductivity

In order to formulate the energy-current density operator (37) in the macroscopic quantities of the group velocity, the specific heat and the phonon lifetime, let us first express $J_{0,qh}{}^l$ in terms of the phonon variables

$$J_{0,qh}{}^l(\mathbf{q}=0,t)=\tfrac{1}{4}iM^{-1}\sum_\rho\sum_{\mathbf{k}pp'}R_\rho{}^l\bar{\eta}_\rho{}^{\mathbf{k}}\eta_\rho{}^{-\mathbf{k}}\tfrac{1}{2}(\omega_{\mathbf{k}p}/\omega_{\mathbf{k}p'})^{1/2}e_{\mathbf{k}p}{}^\alpha e_{\mathbf{k}p'}{}^{\beta\dagger}p^\alpha p^\beta \times V(R_\rho)(a_{\mathbf{k}p}(t)-a_{-\mathbf{k}p}{}^\dagger(t))(a_{-\mathbf{k}p'}(t)+a_{\mathbf{k}p'}{}^\dagger(t)). \quad (56)$$

Taking the derivative of the self-consistent equation (45) with respect to k^l

$$\bar{\omega}_{\mathbf{k}p}\frac{\partial\bar{\omega}_{\mathbf{k}p}}{\partial k^l}\delta_{pp'}=-\frac{i}{4}\frac{1}{M}\sum_\rho R_\rho{}^l\bar{\eta}_\rho{}^{\mathbf{k}}\eta_\rho{}^{-\mathbf{k}}e_{\mathbf{k}p}{}^\alpha e_{\mathbf{k}p}{}^{\beta\dagger}p^\alpha p^\beta \times e^{\frac{1}{2}\bar{\lambda}_{\rho pp}}v(R_\rho)+(\bar{\omega}_{\mathbf{k}p}{}^2-\bar{\omega}_{\mathbf{k}p'}{}^2)e_{\mathbf{k}p}{}^\alpha\frac{\partial e_{\mathbf{k}p'}{}^{\alpha\dagger}}{\partial k^l} \quad (57)$$

we can rewrite Eq. (56) in the form

$$J_{0,qh}{}^l(\mathbf{q}=0,t)=\sum_{\mathbf{k}p}\bar{\omega}_{\mathbf{k}p}(\partial\bar{\omega}_{\mathbf{k}p}/\partial k^l)a_{\mathbf{k}p}(t)a_{\mathbf{k}p}{}^\dagger(t)-\tfrac{1}{4}\sum_{\mathbf{k}pp'}(\bar{\omega}_{\mathbf{k}p}{}^2-\bar{\omega}_{\mathbf{k}p'}{}^2)\left(\frac{\bar{\omega}_{\mathbf{k}p}}{\bar{\omega}_{\mathbf{k}p'}}\right)^{1/2}\times e_{\mathbf{k}p}{}^\alpha\frac{\partial e_{\mathbf{k}p'}{}^{\alpha\dagger}}{\partial k^l}a_{\mathbf{k}p}(t)a_{\mathbf{k}p'}{}^\dagger(t). \quad (58)$$

The first term in (58) represents Peierls' original expression for the energy current density in terms of the phonon frequency, the group velocity $\bar{V}_{\mathbf{k}p}{}^l=\partial\bar{\omega}_{\mathbf{k}p}/\partial k^l$ and the number of phonons. However, we have to keep in mind that these quantities in (58) are now the renormalized ones due to the self-consistent Eq. (45) rather than the harmonic approximated ones used by Peierls. The different polarizations of lattice waves in crystals give rise to the second term in (58). In the expression for the static conductivity the only contributions to the second term in (58) will arise from points of degeneracy in the phonon dispersion and therefore will be neglected here against the dominant first term. The quasiharmonic approximation to the current-current correlation function (36) can then be written

$$F_{p,qh}{}^{ij}(\mathbf{q}=0,t'-t)=\sum_{\mathbf{k}p}\bar{\omega}_{\mathbf{k}p}{}^2\bar{V}_{\mathbf{k}p}{}^i\bar{V}_{\mathbf{k}p}{}^j\times\langle a_{\mathbf{k}p}(t)a_{-\mathbf{k}p}{}^\dagger(t)a_{-\mathbf{k}p}(t')a_{\mathbf{k}p}{}^\dagger(t')\rangle. \quad (59)$$

Using (49) and (50) for the evaluation of the matrix element in (59) we finally derive for the conductivity

$$\mathcal{K}^{ij}(\mathbf{q}=0,\omega\rightarrow 0)=(KT^2)^{-1}\sum_{\mathbf{k}p}\bar{\omega}_{\mathbf{k}p}{}^2\bar{V}_{\mathbf{k}p}{}^i\bar{V}_{\mathbf{k}p}{}^j n(\bar{\omega}_{\mathbf{k}p})$$

$$\times(n(\bar{\omega}_{\mathbf{k}p})+1)(\Gamma(\mathbf{k},p;\bar{\omega}_{\mathbf{k}p}))^{-1}$$

$$=\sum_{\mathbf{k}p}\bar{C}_V(\mathbf{k},p)\bar{V}_{\mathbf{k}p}{}^i\bar{V}_{\mathbf{k}p}{}^j(\Gamma(\mathbf{k},p;\bar{\omega}_{\mathbf{k}p}))^{-1} \tag{60}$$

with the consistent quasiharmonic approximation for the specific heat

$$\bar{C}_V(\mathbf{k},p)=(KT^2)^{-1}\bar{\omega}_{\mathbf{k}p}{}^2 n(\bar{\omega}_{\mathbf{k}p})n((\bar{\omega}_{\mathbf{k}p})+1). \tag{61}$$

Expression (60) for the lattice thermal conductivity is formally completely equivalent to Peierls' result,[18] except that in (60) all quantities are renormalized because of the quasiharmonic self-consistent treatment. To what change in the temperature behavior of the conductivity does this lead? For large temperatures Peierls' expression leads to the well-known $1/T$ law, first discovered by Debye. This behavior of the conductivity is rediscovered in the quasiharmonic approximation for temperatures below the Debye temperature, a region where the phonon frequency and group velocity show a very weak dependence on T. With increasing temperature the temperature dependence of the phonon frequency becomes more and more important and the $1/T$ law is corrected by a factor $1/(1+\alpha T)$. This is obtained by expanding $V(R_\rho)$ to first order in λ_ρ. Here we should keep well in mind that the investigations undertaken so far were carried out by keeping the volume of our system constant. The smeared quasiharmonic potential which leads to thermal expansion in the case of constant pressure, leads to a change of the phonon frequency and group velocity even in the case of constant volume. This gives rise to the T^2 term in the thermal resistivity. On the other hand, a rough examination of Eq. (52) in the case of constant pressure shows that not only the Debye momentum decreases with increasing temperature but also the phonon frequency (given as a function of $\mathbf{k}/k_\Theta$) displays a temperature behavior similar to the one examined in the case of constant volume. Previous calculations which took into account the change of the Debye momentum with temperature could explain the T^2 term in the lattice thermal[19] and electric[20] resistivity. To take into account also the temperature variation of the phonon frequency at constant volume leads to an even stronger increase of the resistivity.

For very large temperatures, and in particular near the critical temperature the phonon frequency shows a rather strong dependence on T. Using relation (54) for the temperature dependence of the mean square fluctuation and assuming that the temperature dependence of $\bar{\omega}_{\mathbf{k}p}$ varies very little with the variation of the wavevector $\mathbf{k}$ and polarization p we obtain the following temperature dependence of $\bar{\omega}_{\mathbf{k}p}$

$$\bar{\omega}_{\mathbf{k}p}{}^2\propto 1+b(T_c-T)^{1/2}. \tag{62}$$

The above assumptions are in good agreement with experiments by Larson *et al.*[21] on the shift of the spectral lines and the width of the phonons as a function of the absolute temperature.

From Eq. (47) we see that the temperature dependence of the phonon width $\Gamma(\mathbf{k},p;\bar{\omega}_{\mathbf{k}p})$ in (60) can be entirely expressed in the temperature dependence of $\bar{\omega}_{\mathbf{k}p}$. Thus the temperature dependence of the conductivity (60) turns out to be proportional to the temperature behavior of a certain power of $\bar{\omega}_{\mathbf{k}p}$. We thus obtain for the temperature behavior of the conductivity in the region just below and at the critical temperature T_c

$$\mathcal{K}=A+B(T_c-T)^{1/2}. \tag{63}$$

Hence, we have the following temperature dependence of the conductivity. Just below the Debye temperature the well known $1/T$ law holds. With increasing temperature the conductivity drops faster and the $1/T$ law is corrected by a factor $1/(1+\alpha T)$. Finally if we come very close to the critical temperature a rapid drop in the conductivity occurs.

V. LATTICE THERMAL CONDUCTIVITY IN THE PAIR APPROXIMATION

After the examination of this part of the anharmonicity in (31) which can be described by autocorrelation functions λ_ρ only and gives rise to a modification of the equilibrium quantities occurring in the conductivity, we now shall investigate the remaining part of the anharmonicity in the pair approximated current-current correlation function. While the autocorrelation function λ_ρ does not depend on the lattice coordinates nor on the absolute time, counted from when the temperature gradient is turned on, the correlation function we have now to deal with, namely $\lambda_{\rho\rho'}{}^Q(\tau)$, does depend on the relative coordinates between two atomic displacements $\mathbf{u}_i(t)$ and $\mathbf{u}_j(t')$. The dissipative mechanism of our system is entirely described by them. The symmetric occurrence of equilibrium and nonequilibrium contributions to (31) can best be studied in the correlation function $\langle v(\mathbf{R}_\rho+\eta_\rho\mathbf{u}_i(t))v(\mathbf{R}_{\rho'}+\eta_{\rho'}\mathbf{u}_j(t'))\rangle$ which is the basic quantity in the description of the current-current correlation function. While this quantity reduces in the quasiharmonic approximation to $V(R_\rho)V(R_{\rho'})$ describing entirely the anharmonic contribution to equilibrium

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[18] R. E. Peierls, *Quantum Theory of Solids* (Clarendon Press, Oxford, England, 1955), p. 40; see also C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed., p. 124.

[19] G. Leibfried and E. Schloemann, Nachr. Akad. Wiss. Göttingen, Math.-Physik. Kl. **IIa**, 71 (1954).

[20] N. F. Mott and H. Jones, *Theory of Metals and Alloys* (Oxford University Press, Oxford, England, 1936), p. 268.

[21] K. E. Larson, S. Holmryd, and U. Dahlborg, in *Proceedings of the Symposium on Inelastic Scattering of Neutrons in Solids and Liquids, Vienna, 1960* (International Atomic Energy Agency, Vienna, 1961), p. 587.

properties, it becomes in the pair approximation

$$\exp[\tfrac{1}{2}\lambda_\rho pp+\lambda_{\rho\rho'}{}^{\mathbf{q}_i-\mathbf{q}_j}(t-t')pp'+\tfrac{1}{2}\lambda_{\rho'}p'p']v(R_\rho)v(R_{\rho'})\,. \tag{64}$$

The combined effect of λ_ρ and $\lambda_{\rho\rho'}{}^{\mathbf{q}_i-\mathbf{q}_j}(t-t')$ in the above correlation function can best be illustrated by examining (64) in terms of the model potential (53), for which we obtain after averaging over the polarizations in λ_ρ, $\lambda_{\rho'}$ and $\lambda_{\rho\rho'}{}^{\mathbf{q}_i-\mathbf{q}_j}(t-t')$

$$W(\lambda,a)=\sum_{(i,j)=(1,2)} d_id_j(-1)^i(-1)^i\left[\frac{c_i{}^2c_j{}^2}{16(x_ix_j-a^2)}\right]^{3/2} \times\exp\left[-\frac{R_\rho{}^2x_j+R_{\rho'}{}^2x_i-2|\mathbf{R}_\rho\cdot\mathbf{R}_{\rho'}|a}{4(x_ix_j-a^2)}\right]. \tag{65}$$

Here we introduce for simplification of the notation

$$x_i=\tfrac{1}{4}c_i{}^2+\lambda_\rho\,,\quad x_j=\tfrac{1}{4}c_j{}^2+\lambda_{\rho'}\,,\quad a=|\lambda_{\rho\rho'}{}^{\mathbf{Q}}(t-t')|$$

with

$$\mathbf{Q}=\mathbf{q}_i-\mathbf{q}_j\,.$$

Before going over to an investigation of $W(\lambda,a)$ respectively of (31) in terms of the natural variables λ_ρ, $\lambda_{\rho'}$, and $\lambda_{\rho\rho'}{}^{\mathbf{Q}}(t-t')$ let us take a look at the correlation of the first kind λ_ρ given in (48). Using a Debye spectrum for the phonon frequency the summation over the wave vectors can be carried out and λ_ρ becomes proportional to $1-(R_\rho k_\Theta)^{-1}\,\mathrm{Si}(R_\rho k_\Theta)$. Since $R_\rho k_\Theta$ is always larger than 2π this quantity is relatively independent of R_ρ and in particular approaches unity for $R_\rho\to\infty$. Therefore, from now on, we will ignore the ρ dependence of λ_ρ and write $\lambda_\rho=\lambda_{\rho'}=\lambda$. For fixed values of λ the term in the first bracket of $W(\lambda,a)$ is an increasing function of a with increasing a. For the main contribution of (65) to the current-current correlation function (31) the same holds for the exponential function in $W(\lambda,a)$. A discussion of the a dependence of this latter term is given in the Appendix. Keeping a constant we see that the term in the first bracket as well as the exponential in $W(\lambda,a)$ decreases as λ increases. From this consideration the effect of the dependence of $W(\lambda,a)$ on a can be described as follows. For $a=0$, the function $W(\lambda,a)$ reduces to the quasiharmonic approximation of the potential-potential correlation function. For any $a\neq0$, the function $W(\lambda,a)$ is always larger than $V(R_\rho)V(R_{\rho'})$, and the quantity $W(\lambda,a)-V(R_\rho)V(R_{\rho'})$ increases as λ increases. The effect of $\lambda_{\rho\rho'}{}^{\mathbf{Q}}(t-t')$ is thus to increase again the total correlation in the second order in the anharmonic potential after its drastic depression by the effect of the correlations of first kind in the lattice potential, described by λ exclusively.

This result, mainly due to the repulsive part of the lattice potential, permits us to neglect the attractive part for further investigation of (31). Keeping the lattice constant fixed in order to prevent the crystal from falling apart, we will be able to derive in this approximation a formula for the conductivity at constant volume. That it is quite sufficient to deal with the repulsive part of the interatomic potential only is illustrated in the investigation of the self-consistent Eq. (52) in Sec. IV.

Remembering that the zero-order term in an expansion of the exponent in (31) is zero[17] we can write the integrand of the current-current correlation function as proportional to

$$\mathrm{I}(\lambda,a)-\mathrm{II}(\lambda)=\left(\frac{1}{x^2-a^2}\right)^{5/2}\sum_{\rho\rho'}R_\rho{}^kR_{\rho'}{}^l\left\{a\left(6-\frac{R_\rho{}^2x+R_{\rho'}{}^2x-2|\mathbf{R}_\rho\cdot\mathbf{R}_{\rho'}|a}{x^2-a^2}\right)+\mathbf{R}_\rho\cdot\mathbf{R}_{\rho'}\right\} \times\exp\left[-\frac{R_\rho{}^2x+R_{\rho'}{}^2x-2|\mathbf{R}_\rho\cdot\mathbf{R}_{\rho'}|a}{4(x^2-a^2)}\right]-\left(\frac{1}{x^2}\right)^{5/2}\sum_{\rho\rho'}R_\rho{}^kR_{\rho'}{}^l\mathbf{R}_\rho\cdot\mathbf{R}_{\rho'}\exp\left[-\frac{R_\rho{}^2+R_{\rho'}{}^2}{4x}\right]. \tag{66}$$

The first term in (66) arises from applying the operator $\mathbf{p}\cdot\mathbf{p}'$ to $W(\lambda,a)$, the second one by setting $a=0$ in the expression thus obtained. A linear expansion of (66) in a/x yields the quasiharmonic approximation

$$\left(\frac{1}{x^2}\right)^{5/2}\sum_{\rho\rho'}R_\rho{}^kR_{\rho'}{}^la\left(6-\frac{R_\rho{}^2+R_{\rho'}{}^2}{x}+\frac{(\mathbf{R}_\rho\cdot\mathbf{R}_{\rho'}{}^2)}{2x^2}\right) \times\exp\left[-\frac{R_\rho{}^2+R_{\rho'}{}^2}{4x}\right] \tag{67}$$

and can be directly compared with (36). Such an approximation of (66) will yield a good result for the conductivity as long as a/x is small. However, since a varies from zero to λ we see that this is not necessarily the case for values of a/x near the upper limit λ/x. In particular for large values of λ this expansion parameter approaches unity. Only for small λ's can this quantity be considered small and only then will the quasiharmonic approximation lead to a good result for the conductivity. Besides the fact that the above expansion in terms of a/x converges badly, we see that the linear term in such an expansion is not even the dominant contribution to (66) for large λ's. In fact, the term (x^2-a^2) in the various denominators of $\mathrm{I}(\lambda,a)$, which does not contribute to the linear expansion of (66) in a/x, nevertheless is the dominant term governing the λ dependence of $\mathrm{I}(\lambda,a)-\mathrm{II}(\lambda)$. This one can see immediately by inserting λ for a, for which this term becomes $(\tfrac{1}{4}c^2)(\tfrac{1}{4}c^2+2\lambda)$ instead of $(\tfrac{1}{4}c^2+\lambda)^2$ in the quasiharmonic approximation of (66). It is obvious that such a result can never be obtained by doing finite-order perturbation theory in lattice

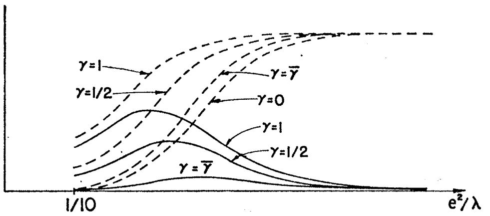

FIG. 4. I(λ,γ) as a function of e^2/λ for various values of γ (dashed curves). The corresponding functions I$(\lambda,\gamma)-$II(λ) are represented by the solid curves.

dynamics and is strictly due to the summation of a whole class of terms in an infinite perturbation expansion.

In order to investigate the λ and a dependence of (66) it is convenient to introduce $a=\gamma\lambda$ and thereby take the boundaries of a into account explicitly by varying γ from zero to unity.

For an examination of the temperature dependence of the conductivity it is sufficient to exploit the λ dependence of (66) which can then be easily transformed by the relation of λ and T discussed in Sec. IV. A comparative study of the λ dependence of (66) and its quasiharmonic approximation will permit us to demonstrate the effect of the lattice anharmonicity as far as it plays a role in the equilibrium and nonequilibrium properties in the lattice thermal conductivity.

Similar considerations as carried out in the investigation of $W(\lambda,a)$ show us that I(λ,γ) [here we denote explicitly the γ dependence in I(λ,a)] is a monotonic increasing function of γ as γ increases. For fixed values of γ, I(λ,γ) is monotonically decreasing with increasing λ. For $\gamma=0$, I(λ,γ) becomes equal to II(λ). A plot of I(λ,γ) and I$(\lambda,\gamma)-$II(λ) is given for various values of γ as a function of e^2/λ in Fig. 4 (e denotes the lattice constant). From the above outline on the derivation of the quasiharmonic approximation (67) from (66) it is now clear how to construct (67) from the result of (66) given in Fig. 4. For very small values of γ the quasiharmonic approximation holds. For such a particular value $\gamma=\bar{\gamma}$ the result is illustrated in Fig. 4. The quasiharmonic result for any particular value of γ is obtained by multiplying I$(\lambda,\bar{\gamma})-$II(λ) by $\gamma/\bar{\gamma}$. This device is demonstrated very clearly in expression (67) where the factor γ appears as multiplicator of a function depending on λ only.

While the maxima of the curves I$(\lambda,\gamma)-$II(λ) move towards larger values of λ/e^2 as λ increases, the maxima of the corresponding quasiharmonic approximation (67) remains at the same value of λ/e^2. This behavior of I$(\lambda,\gamma)-$II(λ) is plotted in Fig. 5, as a function of λ/e^2 for the different steps in our systematic investigation of the current-current correlation function: the harmonic, the quasiharmonic, and the pair approximations. While the set of curves for (67) shows for any value of γ a negative slope near the critical value λ_c/e^2 the main contribution to the pair approximation (66) has positive slopes. Only for small values of γ the slope for I$(\lambda,\gamma)-$II(λ) is negative and the curves of (66) and (67) approach each other the more the smaller γ is. Finally in the harmonic approximation all the curves due to different γ's have positive slopes. It thus becomes clear that the harmonic approximation corresponds to a complete cancellation of the effect of λ and $\lambda_{\rho\rho'}{}^{\mathbf{Q}}(t)$ and thus represents for not too large values of λ a very good result for the lattice thermal conductivity.

The second term in (31), equally important to the first one for small values of λ, can be neglected for large mean square fluctuations. The main contribution to $R_\rho{}^k R_{\rho'}{}^l \mathbf{p}\cdot\mathbf{p}'\langle v(\mathbf{R}_\rho+\eta_\rho\mathbf{u}_i(t))v(\mathbf{R}_{\rho'}+\eta_{\rho'}\mathbf{u}_j(t'))\rangle$ in this case arises from terms of the integrand with $\mathbf{Q}=0$ and $\mathbf{R}_\rho=\mathbf{R}_{\rho'}$. However, in this case the factor in front of the above matrix element

$$\langle\bar{\eta}_\rho \dot{u}_i{}^\alpha(0)\eta_{\rho'}u_j{}^\beta(\tau)\rangle$$

$$=(KT/MN)\sum_{\mathbf{k}p}\cos\tfrac{1}{2}\mathbf{k}\cdot\mathbf{R}_\rho\,\sin\tfrac{1}{2}\mathbf{k}\cdot\mathbf{R}_{\rho'}\,\cos(\mathbf{k}\cdot\mathbf{Q})\bar{\omega}_{\mathbf{k}p}{}^{-1}$$

$$\times e^{-\Gamma(\mathbf{k})\tau}\cos(\bar{\omega}_{\mathbf{k}p}\tau)e_{\mathbf{k}p}{}^\alpha e_{\mathbf{k}p}{}^{\beta\dagger}$$

is zero. For this reason the second term in (31) will now be neglected for a calculation of the conductivity at the dynamical instability.

After carrying out the remaining integrations over the time $t-t'$ and the lattice vector $\mathbf{Q}$ in (31), the lattice thermal conductivity can be written as

$$\mathcal{K}=T^{-1}F(T). \qquad (68)$$

$F(T)$ is obtained by expressing I$(\lambda,\gamma)-$II(λ) in terms of the absolute temperature T and dividing the integrated contribution of I$(\lambda(T),\gamma)-$II$(\lambda(T))$ by T. In Fig. 6 $F(T)$ is illustrated for the harmonic, the quasiharmonic, and the pair approximations. For the first case the phonon lifetime is approximated by a linear temperature behavior.

Below the Debye temperature $F(T)$ varies very little with T and the well known $1/T$ law for the conductivity is confirmed. With increasing temperature the conductivity decreases faster and can be written as $\mathcal{K}\propto 1/T(1+\alpha T)$. This is the region where the quasiharmonic approximation is valid and the change of the $1/T$ law arises entirely from the modification of equilibrium quantities occurring in the expression for the conductivity. The dissipative part of the anharmonicity described by $\lambda_{\rho\rho'}{}^{\mathbf{Q}}(t)$ starts to play a greater and greater role with a further increase of the temperature. Finally at the dynamical instability it has the dominant influence on the temperature behavior of the conductivity

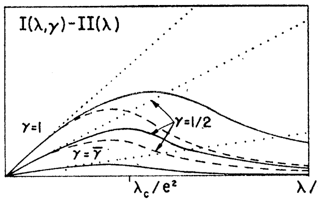

FIG. 5. I$(\lambda,\gamma)-$II(λ) is given as a function of λ/e^2 for the harmonic (dotted lined), the quasiharmonic (dashed lined) and the pair approximation (solid line) for various values of γ.

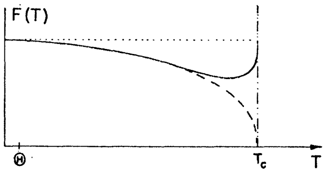

FIG. 6. $F(T)$ is given as a function of T for the harmonic (dotted lined), quasiharmonic (dashed curve) and the pair (solid curve) approximations. The phonon width in the harmonic approximation is assumed to be proportional to T.

and leads to a sharp rise described by

$$\mathcal{K}\propto 1-A(T_c-T)^{1/2}, \tag{69}$$

where A is a constant. For comparison of the oppositely behaving quasiharmonic approach, both approximations for $K(T)$ are plotted in the same diagram Fig. 6. The dependence of the phonon width Γ in the pair approximation for the conductivity no longer occurs in the form $\mathcal{K}\propto 1/\Gamma$. This kind of lifetime-conductivity relation is exclusively due to the static and homogeneous parts of the harmonic, respectively, quasiharmonic approximations, for the lattice thermal conductivity. Next higher order approximations in $\lambda_{\rho\rho'}{}^{Q}(t)$ show in the expression for the conductivity the general dependence of the phonon lifetime

$$\frac{\sum_{i=1}^{n}\Gamma(\mathbf{k}_i)}{(\frac{1}{2}\sum_{i=1}^{n}\Gamma(\mathbf{k}_i))^2+(\sum_{i=1}^{n}(-)^P\omega_{\mathbf{k}_i}{}^2)^2} \tag{70}$$

where $(-)^P$ denotes all possible combinations of plus and minus signs in the sum over $\omega_{\mathbf{k}_i}{}^2$. Only momentum- and energy-conserving processes, where the sum over the phonon frequencies in (69) is zero, give rise to the $1/\Gamma$ dependence of the conductivity. However, these processes restrict our total space of integration over $\mathbf{k}_1, \mathbf{k}_2 \ldots \mathbf{k}_n$ to a negligible fraction of it. The general Γ dependence of the conductivity is therefore not $1/\Gamma$ but rather a complex one, and the study of individual terms of a perturbation expansion of (69) very soon becomes hopeless. In this paper the perturbation expansion is formally summed and the Γ dependence of $\mathcal{K}$ is studied by the dependence of $\lambda_{\rho\rho'}{}^{Q}(t)$ on it.

The result derived in this section, describing the behavior of the conductivity near the dynamical instability takes quite an amount of algebraic exercise and leads finally to a result which is rather an academic one, since every crystal will melt long before it reaches the temperature T_c. Nevertheless, from this result we can conclude that a minimum in the conductivity must occur which is expected to fall in a region of a metastable state. Since high-temperature thermal-conductivity measurements are extremely difficult, only recently has $\mathcal{K}$ been measured for Ge and Si[22] up to the melting point. This region covers roughly the first third of the plot in Fig. 6 and yields a good qualitative agreement with the $1/T(1+\alpha T)$ behavior of the conductivity. Near the melting point the conductivity rises again; this however seems to be due to electron-hole pair diffusion.[23] A more accurate measurement of the intrinsic lattice contribution to the thermal conductivity at the melting point, and perhaps even beyond that up to some metastable state of the crystal, may be possible in the near future.

VI. DIFFUSIVE CORRECTIONS OF THE CONDUCTIVITY

The entire anharmonicity of the interatomic lattice potential taken into account leads to the result for the conductivity discussed in the last two sections. However, from the derivation of the energy-current density via the continuity equation we know that there are more anharmonic contributions to the energy current than have been taken into account so far. The first term in Eq. (8) which has been neglected corresponds to a diffusion current $\mathbf{J}_d$. In the second term in (8) $(q_i-q_j)^l$ is approximated by $(q_i{}^0-q_j{}^0)^l$ in our previous investigation of the conductivity. The remaining term $\eta_\rho\mathbf{u}_i$ in this expression, as well as $\mathbf{J}_d$ has to be studied in the limit of high temperatures where the magnitude of the mean square fluctuations becomes comparable to the lattice constant.

Let us first examine the contribution of $\mathbf{J}_d$ to the conductivity $\langle\mathbf{J}_d(\mathbf{k}=0, t)\mathbf{J}_d(\mathbf{k}=0, t')\rangle$ reduces to the following correlation functions. For the kinetic part of $\mathbf{J}_d$ we obtain the typical term $(\langle\dot{u}_i{}^\alpha(t)\dot{u}_j{}^\beta(t')\rangle)^3$ where α, β denoting the coordinates have to be arranged in the proper way due to $\dot{u}_i{}^k(t)\dot{u}_i{}^\delta(t)u_i{}^\delta(t)$ in $\mathbf{J}_d$. Expressing this correlation function in terms of the phonon variables and after dividing this expression by T^2 the temperature dependent terms in the corresponding expression for the conductivity read

$$T\frac{\Gamma(\mathbf{k}_1)+\Gamma(\mathbf{k}_2)+\Gamma(\mathbf{k}_3)}{(\frac{1}{2}\Gamma(\mathbf{k}_1)+\Gamma(\mathbf{k}_2)+\Gamma(\mathbf{k}_3))^2+(\omega_{\mathbf{k}_1}{}^2\pm\omega_{\mathbf{k}_2}{}^2\pm\omega_{\mathbf{k}_3}{}^2)^2},$$

where all possible combinations of plus and minus signs have to be taken. Apart from the energy-conserving processes which lead to a temperature behavior, T/Γ, we will in general obtain an increasing behavior of the conductivity as the temperature increases. The second correlation function to which $\langle J_dJ_d\rangle$ reduces is

$$\langle\dot{u}_i{}^\alpha(t)\dot{u}_j{}^{\alpha'}(t')\rangle\langle\dot{u}_i{}^\beta(t)\eta_{\rho'}\mathbf{u}_j(t')\cdot\mathbf{p}\rangle\langle\dot{u}_i{}^\gamma(t)\eta_{\rho'}\mathbf{u}_j(t')\cdot\mathbf{p}'\rangle \\ \times\langle v(\mathbf{R}_\rho+\eta_\rho\mathbf{u}_i(t))v(\mathbf{R}_{\rho'}+\eta_{\rho'}\mathbf{u}_j(t'))\rangle.$$

This correlation function is very similar to the one treated in the last section and differs essentially only by the correlation $\langle\dot{u}_i(t)\dot{u}_j(t')\rangle$ which gives rise to an addi-

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[22] C. J. Glassbrenner and G. A. Slack, Phys. Rev. **134**, A1058 (1964).

[23] C. M. Bhandari and A. S. Verma, Phys. Rev. **138**, A288 (1965).

tional factor of T. We thus obtain once again a contribution to the conductivity rising with increasing temperature. Finally the last correlation of $\langle \mathbf{J}_d \mathbf{J}_d \rangle$ which has not yet been taken into account,

$$\langle \dot{u}_i^{\alpha}(t)\eta_\rho \mathbf{u}_i(t)\cdot \mathbf{p}\dot{u}_j^{\alpha'}(t')\eta_{\rho'}\mathbf{u}_j(t')\cdot \mathbf{p}' \rangle \\ \times \langle v(\mathbf{R}_\rho + \eta_\rho \mathbf{u}_i(t)) v(\mathbf{R}_{\rho'} + \eta_{\rho'} \mathbf{u}_j(t')) \rangle ,$$

differs from (31) by a factor $R_\rho^k R_{\rho'}^l \mathbf{p}\cdot\mathbf{p}'$ and thus yields a temperature dependence of $\mathcal{K}$ as discussed in Sec. V.

Similar results are obtained for calculating the correction of the conductivity due to the replacement of $\mathbf{R}_\rho$ by $\mathbf{R}_\rho + \eta_\rho \mathbf{u}_i(t)$ in (25) and finally due to the correlations of $\mathbf{J}_d$ with the intrinsic part of the lattice energy current given by the second term in (8).

This purely qualitative result of additional anharmonic corrections to the lattice thermal conductivity shows again a rising behavior of the conductivity, in particular for high temperatures, and verifies thereby the general qualitative picture of the conductivity given in Sec. V.

VII. CONCLUSION

Using Kubo's formula for the lattice thermal conductivity the effect of the anharmonicity of the interatomic potential on transport phenomena in crystal lattices is examined. A single-phonon lifetime approximation for the current-current correlation function permits us to consider a particular class of terms in an infinite perturbation expansion in the anharmonicity of the correlation function. From the contributions to the anharmonic lattice potential which are diagonal in the atomic displacements we obtain a renormalized lattice potential V, leading to a generalization of Peierl's result for the conductivity. The expression thus obtained is formally equivalent to Peierl's result, but is expressed in terms of the renormalized equilibrium quantities due to V rather than the pure harmonic ones. For temperatures around and just above the Debye temperature the temperature dependence of the conductivity is well described in this approximation by $1/T(1+\alpha T)$. This behavior has been observed recently[22]; but the earlier theoretical explanation cannot be considered conclusive. Pomeranchuk suggested[24] that the taking into account of four-phonon processes will lead to a temperature dependence of the phonon lifetime proportional to $T(1+\gamma T)$ in the high-temperature limit. In a harmonic approximation for the energy current this would yield the expected temperature dependence of the conductivity around the Debye temperature. However, this type of calculation has to be considered with great care. The truncated perturbation expansion of equilibrium as well as nonequilibrium properties in lattice dynamics in terms of the atomic displacements cannot be trusted as previous attempts at calculating these quantities show. Any perturbation expansion reduces to a power series in the absolute temperature and for that reason any truncated perturbation theory does not lead to a good result, especially for high temperatures. The adequate perturbation-theoretic treatment in lattice dynamics is therefore not in terms of the atomic displacements but rather the total anharmonic interatomic potential. Only a result obtained in the latter approach where the ambiguity of truncated perturbation theory is excluded can be considered as justified. In this sense the lattice thermal conductivity is calculated and reproduces the above result for the temperature region around the Debye temperature, but for very different reasons from those given previously. Here the temperature dependence of the phonon frequency causes the correction factor $1/(1+\alpha T)$ to the well known $1/T$ law. Pomeranchuk's argument for deriving this correction factor is based on a truncated perturbation expansion of the phonon lifetime where only three- and four-phonon processes are considered to be relevant. For high temperatures, however, multiphonon processes involving more than four phonons cannot be excluded *a priori* in a calculation of the single-phonon lifetime. From the present detailed investigation of the current-current correlation function we can see that the corrected temperature dependence of the phonon width $T(1+\gamma T)$ does in fact contribute to the correction factor $1/(1+\alpha T)$ in the lattice thermal conductivity for temperatures around the Debye temperature. However, its main contribution arises from the temperature dependence of the phonon frequency.

This example shows that only after we already know the over-all behavior of a particular quantity, calculated in terms of the total anharmonic lattice potential can we then decide whether a particular truncated perturbation expansion of this quantity represents a good result or not. Without having this check, a particular truncated perturbation expansion might lead to a fair qualitative agreement with experiment while the physical reasons for it might be completely different ones. Only in an untruncated perturbation expansion which can formally be re-summed, can one study the influence of various physical effects on the quantity under consideration. In the case of lattice thermal conductivity the influence of the intrinsic equilibrium and nonequilibrium properties of lattice dynamics and the corresponding effect onto each other are studied. This can never be done in the scheme of an ordinary perturbation expansion and valuable physical information may be thereby lost. Here we learn that for temperatures around the Debye temperature the dissipative part of the current-current correlation function can be treated in lowest order and the temperature dependence of the conductivity is mainly governed by the temperature dependence of the equilibrium quantities such as the phonon frequency and group velocity. For higher temperatures, however, the dissipative part of the correlation function has to be treated in all orders in the atomic

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[24] I. Pomeranchuk, Phys. Rev. **60**, 820 (1941).

displacements corresponding to a calculation of the lattice thermal conductivity to lowest order in the anharmonic potential.

A particular cancellation of the depressive effect of the quasiharmonic approach is the result. The correction factor $1/(1+\alpha T)$ in the conductivity is suppressed for high temperatures by the occurrence of a minimum and a subsequent rise of the conductivity at the dynamical instability of the system.

The present examination of the conductivity is carried out by using a model interatomic potential, which is represented by a superposition of two Gaussians. Our qualitative results for the conductivity are not expected to be too sensitive to the model we use. The dominant contribution to the lattice thermal conductivity arises from the soft part of the repulsive term in the lattice potential. This particular portion of the lattice potential however is a common feature of the interatomic potentials in crystal lattices. The effect of a hard core in the lattice potential on the equilibrium properties in lattice dynamics has been studied in Ref. 11. It does not show any qualitative change from the result obtained by the above model potential for the temperature region we are interested in—from the Debye temperature up to the temperature of the dynamical instability.

Studying the current-current correlation function as a function of e^2/λ we obtain the temperature behavior of the conductivity at constant volume by keeping the lattice constant e fixed. If the correlation function is examined as a function of e^2 at constant λ, a rough investigation of the current-current correlation function leads us to expect a temperature dependence of the conductivity at constant pressure similar to the one discussed in this paper. At constant pressure, e^2 will become a function of λ, and since the correlation function in general decreases as e^2 increases, we are led to the above prediction. A shift of the dynamical instability and the minimum of the conductivity can be anticipated. A detailed investigation of this case is yet to be undertaken but is planned for the near future.

Although the result for the lattice thermal conductivity in the region around the dynamical instability will not be accessible to experimental measurements, it represents a useful tool in the determination of the conductivity at high temperatures. In particular, it leads to the prediction of the occurrence of the minimum in the conductivity. Although melting of the crystal is expected to occur at a temperature below the conductivity minimum, a deviation from the $1/T(1+\alpha T)$ behavior of the conductivity should be measurable in this region. For materials which sublime rather than melt, a direct experimental investigation of the minimum in the conductivity might be possible.

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APPENDIX

In Sec. V we make the assumption that the quantity

$$\frac{R_\rho{}^2x+R_{\rho'}{}^2x-2|\mathbf{R}_\rho\cdot\mathbf{R}_{\rho'}|a}{x^2-a^2} \tag{A1}$$

in general decreases with increasing a and is smaller than

$$(R_\rho{}^2+R_{\rho'}{}^2)/x. \tag{A2}$$

In order to show to what extent this assumption is justified, let us consider those values of $\mathbf{R}_\rho$ and $\mathbf{R}_{\rho'}$ for which the above quantities are equal to the arbitrary constant c^2. Wherever the circumference of the circle

$$R_\rho{}^2+R_{\rho'}{}^2=c^2x \tag{A3}$$

lies inside the figure

$$R_\rho{}^2x+R_{\rho'}{}^2x-2|\mathbf{R}_\rho\cdot\mathbf{R}_{\rho'}|a=c^2(x^2-a^2), \tag{A4}$$

the above assumption is fulfilled. By changing the value of c^2 we cover all possibilities of the two lattice vectors $\mathbf{R}_\rho$ and $\mathbf{R}_{\rho'}$ and thus it will be sufficient to carry out our proof for an arbitrary value of the constant c^2.

Keeping in mind that $a=|\lambda_{\rho\rho'}{}^{\mathbf{Q}}(t)|=0$ if at least one of the lattice vectors $\mathbf{R}_\rho$ and $\mathbf{R}_{\rho'}$ is zero, we see immediately that in the neighborhood of $R_\rho=0$ and $R_{\rho'}=0$, (A3) and (A4) coincide. Setting $|\cos(\mathbf{R}_\rho\cdot\mathbf{R}_{\rho'})|=b$ and $a=\alpha\lambda$ (with $0\leq\alpha\leq1$), we can study (A4) in terms of α and b as plotted in Fig. 7. Here the two extreme cases $b=1$, $\alpha=1$ and $b=0$ $\alpha=1$ are illustrated for a fixed

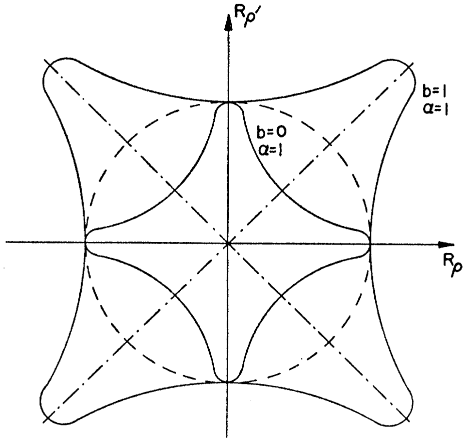

FIG. 7. The two extreme cases of the curve (A4) for a fixed value of λ are represented by the solid curves. As long as the circumference of the circle (dashed curve) lies inside of (A4), the quantity (A1) is always smaller than (A2).

value of λ. The extreme radial separations between the two curves (A4) lie on the line $R_\rho=\pm R_{\rho'}$ and thus the requirement that (A1) should be smaller than (A2) becomes

$$\frac{x^2-\alpha^2\lambda^2}{x-2b\alpha\lambda}>x \quad\text{or}\quad \frac{b}{\alpha}>\frac{\lambda}{2x}.$$

This is fulfilled for any value of λ if $b>\frac{1}{2}\alpha$, and for $\alpha=1$ this leads to $|\cos(\mathbf{R}_\rho,\mathbf{R}_{\rho'})|>\frac{1}{2}$. Already this rough estimation yields a relatively wide angle between $\mathbf{R}_\rho$ and $\mathbf{R}_{\rho'}$ for which our assumption (A1)<(A2) is justified. Taking into account the $\mathbf{R}_\rho$ and $\mathbf{R}_{\rho'}$ dependence in a and considering values of λ which are smaller than λ_c, the allowed angle between R_ρ and $R_{\rho'}$ becomes even larger. Because the current-current correlation function (31) is itself proportional to b^2 the main contribution to it will arise from rather large values of b and in this region our assumption is justified.

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Low-Field de Haas–van Alphen Effect in Gold

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Detailed studies of the de Haas–van Alphen (dHvA) effect in Au single crystals have been carried out with a high-sensitivity torque magnetometer in steady fields up to 40 kG. The angular variations of all of the pertinent dHVA frequencies were determined to better than 0.1%. New low-frequency oscillations have been observed which appear to be associated with a difference frequency resulting from two extremal cross sections on the nearly spherical portion of the Fermi surface. Evidence has been obtained which suggests that the electron g factor for the neck orbits in Au may differ appreciably from the value 2.

I. INTRODUCTION

It has been shown[1] that the Fermi surface in Au, like those in Cu and Ag, can be approximated by a distorted sphere which is multiply connected by necks along the ⟨111⟩ axes. In a recent paper[2] we have reported on a detailed study of the de Haas–van Alphen (dHvA) in effect in Ag, which provided evidence for the existence of two extremal cross sections around the nearly spherical portion, or "belly," of the Fermi surface. In order to examine more closely the fine details of the Fermi surface in Au, we have extended these measurements to several high-purity gold single crystals. As in the case of Ag, we have been able to measure accurately the changes of belly, dog's bone, rosette, and neck oscillations as functions of angle in the {100} and {110} planes. In contrast to the results on Ag, no evidence was found for the existence of two extremal belly orbits in Au when the magnetic field is near the ⟨111⟩ axis. We do, however, find that near the ⟨100⟩ axis there exist low-frequency oscillations similar to those observed in Ag. These may be attributed to the existence of two extremal cross sections of the nearly spherical portion of the Fermi surface.

II. EXPERIMENTAL

The experimental details of the null-deflection torsion balance have been described fully in previous reports.[2,3] The technique was similar to that used in Ag: changes in phase (defined as the ratio F/H_0, where F is the de Haas–van Alphen frequency and H_0 is the applied field) were monitored in a constant magnetic field as the field was rotated about the axis of suspension of the sample. This leads to a very accurate determination of the relative change in frequency, since each change in phase of the belly, for example, corresponds to a change in frequency of ~0.001%. The dominant error in this type of measurement is in the determination of the angle at which the phase is measured. Typically this error can amount to ≈0.05°. This leads to a relative accuracy in frequency of ≈0.01% near a symmetry axis where the phase is not changing rapidly with angle. At angles away from symmetry directions where the phase changes rapidly with angle, the relative accuracy is reduced to ≈0.05%. It is estimated that the absolute accuracy of the frequency values is ±0.6%.

The gold crystal used in the present study was grown in this laboratory by J. Savage and R. Guard, who used the Bridgman technique and a boron nitride crucible. The samples obtained from this crystal exhibited dHvA oscillations much stronger than those prepared in graphite crucibles and showed no experimental evidence

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