tential. Callaway and Glasser[20] have given $V(0)$ due to the uniform charge distribution for the cubic lattice, and we have calculated $V(0)$ for the hexagonal lattice. The results are given below:

$$V(0)_{\text{hcp}} = -(4\pi/\Omega_0)0.06250a_{\text{hcp}}^2,$$
$$V(0)_{\text{bcc}} = -(4\pi/\Omega_0)0.0495536a_{\text{bcc}}^2, \quad \text{(A11)}$$

where a_{hcp} and a_{bcc} are the lattice constants for the two lattices. Taking the atomic volumes to be the same in both the hexagonal and cubic phases and referring both results to the same lattice constant, we obtain a numerical comparison for $V(0)$ for both phases.

$$V(0)_{\text{hcp}} = -(4\pi/\Omega_0)0.0496063a_{\text{bcc}}^2,$$
$$V(0)_{\text{bcc}} = -(4\pi/\Omega_0)0.0495536a_{\text{bcc}}^2. \quad \text{(A12)}$$

While $V(0)_{\text{hcp}}$ is slightly more binding than $V(0)_{\text{bcc}}$, the differences are quite small.

[20] J. Callaway and M. L. Glasser, Phys. Rev. 112, 73 (1958).

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Boltzmann Equation in a Phonon System*

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The Green's function approach is developed to derive the Boltzmann equation for a phonon system having cubic anharmonic interactions. Within the framework of the lowest order scattering process, it is found that the steady-state Boltzmann equation obtained is identical with the Peierls integral equation, except for small correction terms. These correction terms can be absorbed into the transport term by replacing the phonon group velocity appearing in the transport term by the renormalized one, including kinetic and dynamical effects of collisions. Several remarks are made on the generalization of the Boltzmann equation.

I. INTRODUCTION

In this paper, we derive the Boltzmann equation for the phonon distribution only, in a crystal which is subject to a constant and small thermal disturbance such as a temperature gradient and in which phonons interact only with each other through a cubic anharmonic interaction.

Within the framework of the approximation in which only the lowest order scattering process is retained, we can find that the Peierls integral equation[1] for a phonon distribution is to be modified by correction terms. These terms are related to the spatial variation of the phonon distribution, so that they can be interpreted as renormalizing the phonon group velocity in the transport term of the Peierls equation.

The derivation of the Boltzmann equation is carried out here by means of the Green's function method. Kadanoff and Baym[2] have developed the Green's function approach to derive the Boltzmann equation for particle systems of either fermions or bosons subject to a mechanical disturbance. We proceeded initially along similar lines. In the particle case, there are certain difficulties concerning the choice of the boundary conditions for the Green's function defined in a real time domain. However, the thermodynamical Green's function defined for imaginary times satisfies definite boundary conditions. Then, using the relationship between the real-time and the imaginary-time Green's functions, and converting the equation of motion for the imaginary-time Green's function into that for the real-time Green's function, the Boltzmann equation for a particle distribution function results. Thus, the essential part of this derivation of the Boltzmann equation appears to rest on the unique relationship between the real-time and the imaginary-time Green's functions; and this, in turn, is determined by the assumptions imposed on the asymptotic behavior of the system at the time $t = -\infty$ at which the mechanical disturbance was turned on adiabatically.

On the other hand, in the present case of phonons, we have a rather different situation in several respects. First, in addition to the wave nature of phonons, the cubic anharmonic interactions do not conserve the number of phonons. Second, the external disturbance applied to the system is not a mechanical one. To cope with this situation, we have had to use arguments rather different from those used in the particle case.

In Sec. II, we introduce a "nonequilibrium" phonon Green's function D, which is defined by the statistical average of the complex time correlation of "displacement" operators. This nonequilibrium phonon Green's function is different from the usual definition of a phonon Green's function in that no specific functional form is assumed for the density matrix specifying the

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[1] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, Oxford, 1955).
[2] L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962).

statistical nature of the system. Instead, the definition of D is supplemented by assigning physically reasonable analytic and asymptotic properties to it. The equations of motion for D are given in Sec. III, and their derivation is described in the Appendix.

Since we are then interested in obtaining a Boltzmann equation for the phonon distribution, it is necessary to construct the wave packet of phonons. For this purpose, we construct a "phonon number-density" Green's function, G. Then (Sec. IV), the Wigner-like distribution function for a phonon is easily expressed in terms of G.

Were we able to construct G directly, the calculations would be completed, but owing to the wave nature of phonons, the equation of motion for G becomes overly complicated to be handled directly. For this reason, we work with the equation of motion for D, instead of working directly with that for G. As is shown in Sec. IV, there is a simple relation between G and D, which serves to transform the equations of motion for D into the Boltzmann equation for the phonon-distribution function.

The important basic assumptions adopted to derive the Boltzmann equation are as follows:

(A) The nonequilibrium behavior of the system, which is our interest, is completely described by the "nonequilibrium" Green's functions.

(B) In the sufficiently remote future, say T, which will be eventually put equal to $+\infty$, the system tends to an "equilibrium state," which will be characterized by analytic properties of "equilibrium" phonon Green's functions.

(C) At the present time t_0, the system is reasonably close to the equilibrium state. Accordingly, we are essentially concerned with linear phenomena.

While these conditions are shown to be sufficient to lead to the Boltzmann equation it is not demonstrated that they are unique, nor general.

The mathematical procedure to derive the Boltzmann equation is presented in Sec. V, where we focus our argument to the lowest-order scattering process of phonons, and also to the "steady-state" case where the phonon-distribution function is independent of time t_0.

Section VI is devoted to discussions of the result obtained and the possible generalization of Peierls' integral equation.

II. PHONON GREEN'S FUNCTIONS DESCRIBING THE NONEQUILIBRIUM STATE

Throughout the present paper, we put $\hbar=1$ and take the volume of the system to be unity. The Hamiltonian of the system is taken to be

$$H=\sum_k \omega_k a_k^+ a_k+\sum_{k_1,k_2,k_3} \tfrac{1}{3}V(k_1,k_2,k_3)A_{k_1}A_{k_2}A_{k_3}. \quad (2.1)$$

In this expression, the operators a_k and a_k^+ are phonon annihilation and creation operators, respectively. The suffix k represents the wave vector, $\mathbf{k}$, and the polarization index j of phonon, i.e., $k\equiv(\mathbf{k},j)$. In what follows, we also use the conventional notation that $-k\equiv(-\mathbf{k},j)$. The operator A_k, which is the displacement operator, is defined by

$$A_k=(1/2\omega_k)^{1/2}(a_k+a_{-k}^+). \quad (2.2a)$$

Defining the conjugate operator B_k by

$$B_k=-i(\omega_k/2)^{1/2}(a_k-a_{-k}^+), \quad (2.2b)$$

we find that these operators satisfy the following relations:

$$A_{-k}=A_k^+, \quad B_{-k}=B_k^+, \quad (2.3a)$$

$$[A_k,A_{k'}]=[B_k,B_{k'}]=0, \quad (2.3b)$$

$$[A_k,B_{k'}]=i\Delta(k+k'), \quad (2.3c)$$

where

$$\Delta(k+k')\equiv\delta_{j,j'}\delta(\mathbf{k}+\mathbf{k}') \bmod \mathbf{K} \quad (2.4)$$

($\mathbf{K}$ is an arbitrary reciprocal lattice vector).

The coefficients $V(k_1,k_2,k_3)$ in the second term of Eq. (2.1) are the Fourier transforms of the third-order atomic force constant, and related to the analogous coefficients Φ defined by Born and Huang[3] by[4]

$$V(k_1,k_2,k_3)=(\tfrac{1}{2}N^{1/2})\Phi(k_1,k_2,k_3)\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3). \quad (2.5)$$

The coefficients $V(k_1,k_2,k_3)$ have the well-known properties that they are unchanged by permutation of their arguments, and are changed into their complex conjugate by an inversion of all their wave vectors.

We introduce "nonequilibrium" phonon Green's functions by

$$D(p,t;p',t')=D^{>}(p,t;p',t') \quad \text{for} \quad 0>\operatorname{Im}(t-t_0)-\operatorname{Im}(t'-t_0)>-\beta, \quad (2.6a)$$

$$=D^{<}(p,t;p',t') \quad \text{for} \quad \beta>\operatorname{Im}(t-t_0)-\operatorname{Im}(t'-t_0)>0, \quad (2.6b)$$

where

$$D^{>}(p,t;p',t')\equiv-i\langle A_p^+(t)A_{p'}(t')S\rangle/\langle S\rangle, \quad (2.7a)$$

$$D^{<}(p,t;p',t')\equiv-i\langle A_{p'}(t')A_p^+(t)S\rangle/\langle S\rangle, \quad (2.7b)$$

$$S=T\exp\left\{i\sum_k\int_{t_0}^{t_0-i\beta}dtJ_k(t)A_k(t)\right\}, \quad (2.8)$$

$$A_p(t)=\exp(iHt)A_p\exp(-iHt), \quad (2.9)$$

$$\langle\cdots\rangle=\operatorname{trace}\{\rho\cdots\}. \quad (2.10)$$

In Eq. (2.10), ρ is a "nonequilibrium" density matrix describing the system under consideration. In this definition of D, all the time arguments, t and t', take com-

[3] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954), p. 217.

[4] A. A. Maradudin and A. E. Fein, Phys. Rev. **128**, 2589 (1962).

plex values on the line from t_0 to $t_0-i\beta$, where t_0 is a real number and denotes the present time and β is identified with $1/kT$ asymptotically. The symbol T in the expression (2.8) means to rearrange the operators in order of magnitude of the imaginary parts of the time arguments, in the same way as is expressed by Eqs. (2.6) and (2.7). The generating operator S has been introduced for mathematical convenience to derive the equations of motion for D. The source parameter $J_k(t)$ may be assumed to be an infinitesimally small quantity which vanishes as $t\rightarrow+\infty$.

We also need the "equilibrium" phonon Green's function, D_{eq}, which is defined by the same expressions (2.6) and (2.7), as D, except that S is put equal to unity and the density matrix ρ is replaced by the grand canonical equilibrium density matrix with chemical potential $\mu=0$,

$$\rho_{\text{eq}}=\exp(-\beta H)/\text{trace}\exp(-\beta H)\,. \tag{2.11}$$

Then, we see that $D_{\text{eq}}{}^{>}(p,t;p',t')$ and $D_{\text{eq}}{}^{<}(p,t;p',t')$ have the following properties. (1) They depend only on the difference of the time arguments, $t-t'$. (2) They are diagonal in wave vectors $\mathbf{p}$, because the Hamiltonian H has the translational symmetry of the crystal. (3) They are analytic in the restricted domains of complex time plane, $0>\text{Im}(t-t')>-\beta$ and $\beta>\text{Im}(t-t')>0$, respectively. (4) They satisfy the periodic boundary condition

$$D_{\text{eq}}{}^{>}(p,\,t-t')=D_{\text{eq}}{}^{<}(p,\,t-t'+i\beta)\,, \tag{2.12}$$

which can be proved by using the cyclic invariance of the trace and recalling that the chemical potential for phonons is zero.[2] (5) We also assign the property to $D_{\text{eq}}{}^{>,<}$ that they are diagonal in the polarization index of photons.

In the definition of the nonequilibrium Green's function D, the density matrix ρ describing the system is obviously not taken to be the same canonical form as Eq. (2.11). Instead of taking any specific functional form at first for the density matrix ρ, we assign the following properties to $D^{>,<}$, in accordance with the basic assumptions mentioned in the introduction. (1) $D^{>,<}(p,t;p',t')$ is dependent only on $t-t'$, analytic in the same domains of complex time plane as $D_{\text{eq}}{}^{>,<}$ and diagonal in the polarization index of phonons. (2) As for the wave-vector dependence, we regard $D^{>,<}(p,t;p',t')$ as being sharply peaked functions about $\frac{1}{2}(\mathbf{p}+\mathbf{p}')$ with small spread around it. (3) $D^{>,<}$ is independent of t_0. Strictly speaking, the nonequilibrium Green's function describing the nonequilibrium behavior of the system should be dependent on the choice of the present time t_0. However, since we consider the steady-state case where the external thermal disturbance is constant, we neglect the t_0 dependence of $D^{>,<}$ in the present problem. Thus, though the derivations following contain apparently separate dependence on t_1 and t_2, this is done for mathematical convenience and any dependence on $t_0=\frac{1}{2}(t_1+t_2)$ is to be suppressed.

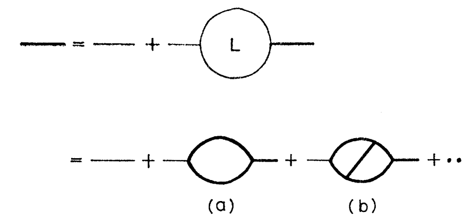

FIG. 1. A schematic representation of the equation of motion for D.

III. EQUATIONS OF MOTION FOR D

Using Eqs. (2.3) and the symmetry properties of the coefficients, $V(k_1,k_2,k_3)$, of the cubic interactions, we obtain the equations of motion for the operators $A_p(t)$ and $B_p(t)$ as follows:

$$\dot{A}_p=B_p\,, \tag{3.1a}$$

$$\dot{B}_p=-\omega_p{}^2A_p-\sum_{k_1,k_2,k_3}V(k_1,k_2,k_3)\Delta(k_1+p)A_{k_3}A_{k_2}\,. \tag{3.1b}$$

By use of these equations, we can derive the equations of motion for D, which are written as

$$\begin{aligned}&[(\partial^2/\partial t_1{}^2)+\omega_{p_1}{}^2]D(p_1,t_1;p_2,t_2)\\&\quad=-\delta(it_1-it_2)\Delta(p_1-p_2)-\sum_{k_1,k_2,k_3}V(k_1,\,-k_2,\,k_3)\\&\qquad\times\Delta(k_1-p_1)R(-k_2,\,t_1;\,k_3,\,t_1;\,p_2,\,t_2)\end{aligned} \tag{3.2a}$$

and

$$\begin{aligned}&[(\partial^2/\partial t_2{}^2)+\omega_{p_2}{}^2]D(p_1,t_1;p_2,t_2)\\&\quad=-\delta(it_1-it_2)\Delta(p_1-p_2)-\sum_{k_1,k_2,k_3}V(-k_1,\,k_2,\,-k_3)\\&\qquad\times\Delta(k_1-p_2)R(-p_1,\,t_1;\,k_2,\,t_2;\,-k_3,\,t_2)\,.\end{aligned} \tag{3.2b}$$

The second-order time derivatives on the left-hand side of Eq. (3.2) are carried out along the line from t_0 to $t_0-i\beta$ in the complex time plane. On the right-hand side of Eq. (3.2), the first terms come from the differentiation of the chronological ordering symbol T in the expression of D. In the second terms, the new Green's function R is defined by

$$\begin{aligned}&R(p_1,t_1;\,p_2,t_2;\,p_3,t_3)\\&\qquad\equiv-i\langle T\{A_{p_1}(t_1)A_{p_2}(t_2)A_{p_3}(t_3)S\}\rangle/\langle S\rangle\,.\end{aligned} \tag{3.3}$$

In the Appendix, it is shown that the new function R, which is a functional of D, can be expressed in terms of D. Therefore, we can rewrite Eq. (3.2a), for example, in the following form.

$$\begin{aligned}&[(\partial^2/\partial t_1{}^2)+\omega_{p_1}{}^2]D(p_1,t_1;p_2,t_2)\\&\quad=-\Delta(p_1-p_2)\delta(it_1-it_2)+\sum_q\int_{t_0}^{t_0-i\beta}d\tau L(p_1,t_1;\,q,\tau)\\&\qquad\times D(q,\tau;\,p_2,t_2)\,.\end{aligned} \tag{3.4}$$

Here L satisfies the following equation:

$$L(p_1,t_1;q,\tau)=-\sum_{k_1,k_2,k_3}\Delta(k_1-p_1)V(k_1,-k_2,k_3)$$
$$\times\left\{\bar{A}_{-k_2}(t_1)\delta(q+k_3)\delta(\tau-t_1)+i\sum_{q_2,q_3}\int_{t_0}^{t_0-i\beta}d\tau_2\int_{t_0}^{t_0-i\beta}d\tau_3\Gamma(-q_3,\tau_3;q_2,\tau_2;-q,\tau)\right.$$
$$\left.\times D(q_3,\tau_3;k_3,t_1)[D(k_2,t_1;q_2,\tau_2)+i\bar{A}_{q_2}(\tau_2)\bar{A}_{-k_2}(t_1)]\right\}, \quad (3.5)$$

where

$$\Gamma(-q_3,\tau_3;q_2,\tau_2;-q,\tau)$$
$$\equiv-\delta D^{-1}(-q_3,\tau_3;q,\tau)/\delta\bar{A}_{q_2}(\tau_2)$$
$$=-\delta L(-q_3,\tau_3;q,\tau)/\delta\bar{A}_{q_2}(\tau_2), \quad (3.6)$$

$$\bar{A}_q(\tau)\equiv\langle T\{A_q(\tau)S\}\rangle/\langle S\rangle. \quad (3.7)$$

The quantity $\bar{A}_q(\tau)$ defined by Eq. (3.7) is not, *a priori*, taken to be vanishing, because there exists spatial inhomogeneity in the system. As a matter of fact, $\bar{A}_q(\tau)$ can be regarded as representing a dynamical phonon field produced by the creation (or destruction) of phonons. The time dependence of this phonon field destroys the stationarity of the phenomena, introducing a t_0 dependence into the formulation. Eventually, we restrict consideration to negligible t_0 dependence, but we may drop the terms including $\bar{A}_q(\tau)$ explicitly only after carrying out formally the proper evaluation of D. Actually, in order to obtain the expression for L, we iterate Eq. (3.5) by using Eq. (3.6) and then drop the terms still including $\bar{A}_q(\tau)$ explicitly. Thus, we can, in principle, obtain an expansion of L in terms of D's, which is not written down here explicitly. The structure of the equation of motion (3.4) is shown schematically in Fig. 1, where the heavy solid line represents D and the light solid line represents the "noninteracting" phonon Green's function D_0 defined by

$$[(\partial^2/\partial t_1^2)+\omega_{p_1}^2]D_0(p_1,t_1;p_2,t_2)$$
$$=-\Delta(p_1-p_2)\delta(it_1-it_2). \quad (3.8)$$

IV. PHONON NUMBER-DENSITY GREEN'S FUNCTION G

To derive the Boltzmann equation for the phonon distribution, we must consider wave packets of phonons. These may be studied by introducing the "phonon number-density" Green's functions, which are defined by

$$G(p_1,t_1;p_2,t_2)=G^>(p_1,t_1;p_2,t_2)\quad\text{for}$$
$$0>\mathrm{Im}(t_1-t_0)-\mathrm{Im}(t_2-t_0)>-\beta, \quad (4.1a)$$
$$=G^<(p_1,t_1;p_2,t_2)\quad\text{for}$$
$$\beta>\mathrm{Im}(t_1-t_0)-\mathrm{Im}(t_2-t_0)>0, \quad (4.1b)$$

where

$$G^>(p_1,t_1;p_2,t_2)=\langle a_{p_1}^+(t_1)a_{p_2}(t_2)S\rangle/\langle S\rangle, \quad (4.2a)$$
$$G^<(p_1,t_1;p_2,t_2)=\langle a_{p_1}(t_2)a_{p_2}^+(t_1)S\rangle/\langle S\rangle. \quad (4.2b)$$

Then, we can define the Wigner-like[5] distribution function for phonons in terms of $G^>$ as follows.

$$N(\mathbf{p};j;\mathbf{R})$$
$$=\sum_{\kappa}\exp(-i\boldsymbol{\kappa}\cdot\mathbf{R})G^>\left(\mathbf{p}+\frac{\boldsymbol{\kappa}}{2},j,t_1;\mathbf{p}-\frac{\boldsymbol{\kappa}}{2},j,t_2\right)\Bigg|_{\substack{t_1\to t_0-i0\\ t_2\to t_0-i0.}} \quad (4.3)$$

Within the framework of the present approximation, in which the t_0 dependence of the Green's function is neglected, the distribution function $N(\mathbf{p};j;\mathbf{R})$ is independent of time.

As was mentioned in the introduction, it is hard to work directly with the equations of motion for G, which could not be obtained in a simple form. Fortunately, there is a simple relation between G and D,

$$G(p_1,t_1;p_2,t_2)$$
$$=\frac{1}{2i}(\omega_{p_1}\omega_{p_2})^{-1/2}\Delta(p_1-p_2)\delta(it_1-it_2)$$
$$+\frac{i}{2}(\omega_{p_1}\omega_{p_2})^{-1/2}\left(\frac{\partial}{\partial t_1}+i\omega_{p_1}\right)\left(\frac{\partial}{\partial t_2}-i\omega_{p_2}\right)$$
$$\times D(p_1,t_1;p_2,t_2). \quad (4.4)$$

This relation is easily verified if we write the expression of G in terms of A_p and B_p, and compare it with the right-hand side of Eq. (4.4), where Eqs. (3.1) are used for the time derivatives.

In the next section, Eqs. (4.3) and (4.4) are used to transform the equations of motion for D into that for the phonon-distribution function N.

V. DERIVATION OF THE BOLTZMANN EQUATION

The deviation of the system from the equilibrium state is described by the difference of the nonequilibrium Green's function from the equilibrium one. Denoting this difference by $\Delta D=D-D_{\mathrm{eq}}$ (or $\Delta G=G-G_{\mathrm{eq}}$), we linearize the equations of motion (3.2) with respect to ΔD (or ΔG).

In what follows, we focus our argument only to the lowest-order scattering process, which is represented by diagram (a) in Fig. 1.

[5] E. P. Wigner, Phys. Rev. 40, 749 (1932).

We apply the differential operator $[(\partial/\partial t_1)-i\omega_{p_1}]$ on both sides of Eq. (4.4), and use Eq. (3.4) to eliminate the second-order time derivatives of D. Then, we obtain the equation which governs the first-order time derivatives of G, i.e., $(\partial/\partial t_1-i\omega_{p_1})G(p_1,t_1;\,p_2,t_2)$, whereas the right-hand side of the equation is still written in terms of D's. Subtracting the corresponding equation of motion for $G_{\rm eq}$ from the equation of motion for G obtained, we are led to the equation of motion for ΔG, which is written as

$$[(\partial/\partial t_1)-i\omega_{p_1}]\Delta G(p_1,t_1;\,p_2,t_2)=\tfrac{1}{2}(\omega_{p_1}\omega_{p_2})^{-1/2}\sum_{k_2,k_3}\sum_{q_1,q_2,q_3}V(p_1,-k_2,k_3)V(-q_1,q_2,-q_3)$$
$$\times\int_{t_0}^{t_0-i\beta}d\tau[(\partial/\partial t_2)-i\omega_{p_2}]\Delta\{D(k_2,t_1;\,q_2,\tau)D(q_3,\tau;\,k_3,t_1)D(q_1,\tau;\,p_2,t_2)\}\,. \quad (5.1a)$$

For the lowest order scattering process represented by the diagram (a) in Fig. 1, there appears the product of three D's in the right-hand side of Eq. (5.1a). The symbol $\Delta\{\cdots\}$ is to retain only linear terms of ΔD.

Similarly, applying the operator $[(\partial/\partial t_2)+i\omega_{p_2}]$ on both sides of Eq. (4.4), and using Eq. (3.2b), we obtain

$$[(\partial/\partial t_2)+i\omega_{p_2}]\Delta G(p_1,t_1;\,p_2,t_2)=\tfrac{1}{2}(\omega_{p_1}\omega_{p_2})^{-1/2}\sum_{k_2,k_3}\sum_{q_1,q_2,q_3}V(-p_2,k_2,-k_3)V(q_1,-q_2,q_3)$$
$$\int_{t_0}^{t_0-i\beta}d\tau[(\partial/\partial t_1)+i\omega_{p_1}]\Delta\{D(p_1,t_1;\,q_1,\tau)D(q_2,\tau;\,k_2,t_2)D(k_3,t_2;\,q_3,\tau)\}\,. \quad (5.1b)$$

The Boltzmann equation is then derived by the following procedure. To begin with, we assume that $i(t_1-t_0)>i(t_2-t_0)$, so that it suffices to consider $\Delta G^>(p_1t_1;\,p_2t_2)$.

(1) Add the two equations (5.1a) and (5.1b). Then the left-hand side is given by

$$-i(\omega_{p_1}-\omega_{p_2})\Delta G^>(p_1,t_1;\,p_2,t_2), \quad (5.2)$$

because the other terms, $(\partial/\partial t_1)\Delta G^>$ and $(\partial/\partial t_2)\Delta G^>$, cancel each other on account of the fact that $\Delta G^>\times(p_1t_1;\,p_2t_2)$ depends only on t_1-t_2.

(2) Consider the integral appearing on the right-hand side of the combined equation. Let Γ be the complex time domain enclosed by straight line segments (C_0,C_1,C_2,C_3) illustrated in Fig. 2. Since both $D^{>,<}$ and $D_{\rm eq}{}^{>,<}$ have no singularity in Γ, the integral along $C_0(t_0\to t_0-i\beta)$ can be replaced by the integral along C_1, C_2 and C_3 by making use of Cauchy's theorem. Moreover, since we assume that in sufficiently remote future the system approaches the equilibrium state, we can put $\Delta D^{>,<}$ equal to zero along the path C_2 in the limit of $T\to+\infty$. Therefore the net contribution of this integral comes only through the integrals along the paths C_1 and C_3. Thus, in the limit of $T\to+\infty$ the integral along the path C_0 is changed to

$$\int_{t_0}^{t_0-i\beta}d\tau\Delta\{D(q_1;\,\tau;\,p_2,t_2)D(k_2,t_1;\,q_2,\tau)D(q_3,\tau;\,k_3,t_1)\}\to\lim_{T\to\infty}\int_{t_0}^{T}d\tau\Delta\{D^<(q_1,\tau;\,p_2,t_2)D^>(k_2,t_1;\,q_2,\tau)D^<(q_3,\tau;\,k_3,t_1)\}$$
$$-\lim_{T\to\infty}\int_{t_0-i\beta}^{T-i\beta}d\tau\Delta\{D^>(q_1,\tau;\,p_2,t_2)D^<(k_2,t_1;\,q_2,\tau)D^>(q_3,\tau;\,k_3,t_1)\}\,. \quad (5.3)$$

The other integral appearing in Eq. (5.1b) is also changed in the same manner.

(3) Take the limit of

$$t_2\to t_0-i0,\quad t_1\to t_0-i0,\quad [i(t_1-t_0)>i(t_2-t_0)].$$

Then, all the time arguments of the Green's functions appearing on both sides of the equation take values on the real axis or the axis parallel to the real axis. Along these axes we can introduce the Fourier transform of the Green's functions by

$$G^{>,<}(t)=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}G^{>,<}(\omega)e^{-i\omega t}, \quad (5.4a)$$

$$D^{>,<}(t)=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}D^{>,<}(\omega)e^{-i\omega t}. \quad (5.4b)$$

Thus, we can write the equation in terms of the Fourier transforms.

(4) Linearize the right-hand side of the equation with respect to $\Delta D^{>,<}$. Note that the term $\Delta\{\cdots\}$ of Eqs. (5.1a) and (5.1b) gives rise to three terms, each of which consists of the product of $\Delta D^{>,<}$ and two $D^{>,<}$'s. We replace these two $D^{>,<}$'s by $D_{\rm eq}{}^{>,<}$'s. In the further reduction of the equation, we make use of the

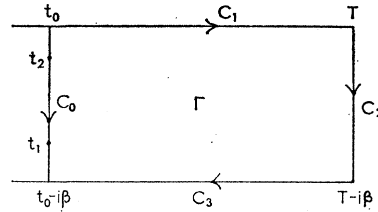

FIG. 2. The path of the integration appearing on the right-hand side of Eq. (5.1a) or Eq. (5.1b).

properties of $D_{\rm eq}^{>,<}$, which were mentioned in Sec. II, and the symmetry properties of the coefficients $V(k_1,k_2,k_3)$.

It is convenient to introduce the mean and relative wave vectors by

$$\mathbf{p}=\tfrac{1}{2}(\mathbf{p}_1+\mathbf{p}_2)\,, \tag{5.5a}$$

and

$$\boldsymbol{\kappa}=\mathbf{p}_1-\mathbf{p}_2\,, \tag{5.5b}$$

and denote $\Delta D^{>,<}(p_1,p_2;\omega_1)$ by $\Delta D^{>,<}(\mathbf{p},\boldsymbol{\kappa};j_1;\omega_1)$. Noticing that the p_1 and p_2 refer to the same polarization index j_1, we rewrite ω_{p_1} and ω_{p_2} as $\omega(\mathbf{p}+\frac{1}{2}\boldsymbol{\kappa},j_1)$ and $\omega(\mathbf{p}-\frac{1}{2}\boldsymbol{\kappa},j_1)$, respectively.

As a result, we obtain the equation of motion, which is given by

$$\begin{aligned}
&(-i)\left\{\omega\left(\mathbf{p}+\frac{\boldsymbol{\kappa}}{2},j_1\right)-\omega\left(\mathbf{p}-\frac{\boldsymbol{\kappa}}{2},j_1\right)\right\}\int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\Delta G^{>}(\mathbf{p},\boldsymbol{\kappa};j_1;\omega_1)\\
&=\frac{(-i)}{2}\left\{\omega\left(\mathbf{p}+\frac{\boldsymbol{\kappa}}{2},j_1\right)\omega\left(\mathbf{p}-\frac{\boldsymbol{\kappa}}{2},j_1\right)\right\}^{-1/2}\sum_{\mathbf{k}_2,\mathbf{k}_3}\sum_{j_2,j_3}\iiint_{-\infty}^{+\infty}\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\lim_{T\to+\infty}\\
&\quad\times\Bigg\{[\Delta D^{>}(\mathbf{p},\boldsymbol{\kappa};j_1;\omega_1)-\Delta D^{<}(\mathbf{p},\boldsymbol{\kappa};j_1;\omega_1)e^{\beta\omega_1}]D_{\rm eq}{}^{<}(\mathbf{k}_2,j_2;\omega_2)D_{\rm eq}{}^{>}(\mathbf{k}_3,j_3;\omega_3)\\
&\quad\times\Bigg[\left\{\omega_1-\omega\left(\mathbf{p}-\frac{\boldsymbol{\kappa}}{2},j_1\right)\right\}\left|V\left(\mathbf{p}+\frac{\boldsymbol{\kappa}}{2},j_1;-\mathbf{k}_2,j_2;\mathbf{k}_3,j_3\right)\right|^2\int_0^{T-t_0}d\tau e^{-i(\omega_1-\omega_2+\omega_3)\tau}\\
&\quad+\left\{\omega_1-\omega\left(\mathbf{p}+\frac{\boldsymbol{\kappa}}{2},j_1\right)\right\}\left|V\left(\mathbf{p}-\frac{\boldsymbol{\kappa}}{2},j_1;-\mathbf{k}_2,j_2;\mathbf{k}_3,j_3\right)\right|^2\int_0^{T-t_0}d\tau e^{+i(\omega_1-\omega_2+\omega_3)\tau}\Bigg]\\
&\quad+[\Delta D^{<}(\mathbf{k}_2,\boldsymbol{\kappa};j_2;\omega_2)-\Delta D^{>}(\mathbf{k}_2,\boldsymbol{\kappa};j_2;\omega_2)e^{-\beta\omega_2}]D_{\rm eq}{}^{>}(\mathbf{k}_3,j_3;\omega_3)\\
&\quad\times V\left(\mathbf{p}+\frac{\boldsymbol{\kappa}}{2},j_1;-\mathbf{k}_2-\frac{\boldsymbol{\kappa}}{2},j_2;\mathbf{k}_3,j_3\right)V^*\left(\mathbf{p}-\frac{\boldsymbol{\kappa}}{2},j_1;-\mathbf{k}_2+\frac{\boldsymbol{\kappa}}{2},j_2;\mathbf{k}_3,j_3\right)\\
&\quad\times\Bigg[\left\{\omega_1-\omega\left(\mathbf{p}-\frac{\boldsymbol{\kappa}}{2},j_1\right)\right\}D_{\rm eq}{}^{>}\left(\mathbf{p}-\frac{\boldsymbol{\kappa}}{2},j_1;\omega_1\right)\int_0^{T-t_0}d\tau e^{-i(\omega_1-\omega_2+\omega_3)\tau}\\
&\quad+\left\{\omega_1-\omega\left(\mathbf{p}+\frac{\boldsymbol{\kappa}}{2},j_1\right)\right\}D_{\rm eq}{}^{>}\left(\mathbf{p}+\frac{\boldsymbol{\kappa}}{2},j_1;\omega_1\right)\int_0^{T-t_0}d\tau e^{+i(\omega_1-\omega_2+\omega_3)\tau}\Bigg]\\
&\quad+[\Delta D^{>}(\mathbf{k}_3,\boldsymbol{\kappa};j_3;\omega_3)-\Delta D^{<}(\mathbf{k}_3,\boldsymbol{\kappa};j_3;\omega_3)e^{\beta\omega_3}]D_{\rm eq}{}^{<}(\mathbf{k}_2,j_2;\omega_2)\\
&\quad\times V\left(\mathbf{p}+\frac{\boldsymbol{\kappa}}{2},j_1;-\mathbf{k}_2,j_2;\mathbf{k}_3-\frac{\boldsymbol{\kappa}}{2},j_3\right)V^*\left(\mathbf{p}-\frac{\boldsymbol{\kappa}}{2},j_1;-\mathbf{k}_2,j_2;\mathbf{k}_3+\frac{\boldsymbol{\kappa}}{2},j_3\right)\\
&\quad\times\Bigg[\left\{\omega_1-\omega\left(\mathbf{p}-\frac{\boldsymbol{\kappa}}{2},j_1\right)\right\}D_{\rm eq}{}^{>}\left(\mathbf{p}-\frac{\boldsymbol{\kappa}}{2},j_1;\omega_1\right)\int_0^{T-t_0}d\tau e^{-i(\omega_1-\omega_2+\omega_3)\tau}\\
&\qquad\qquad+\left\{\omega_1-\omega\left(\mathbf{p}+\frac{\boldsymbol{\kappa}}{2},j_1\right)\right\}D_{\rm eq}{}^{>}\left(\mathbf{p}+\frac{\boldsymbol{\kappa}}{2},j_1;\omega_1\right)\int_0^{T-t_0}d\tau e^{+i(\omega_1-\omega_2+\omega_3)\tau}\Bigg]\Bigg\}.
\end{aligned}\tag{5.6}$$

One of the important features of this equation is that if $\Delta D^{>,<}$ satisfies

$$\Delta D^{>}(\mathbf{p},\boldsymbol{\kappa};j;\omega)=\Delta D^{<}(\mathbf{p},\boldsymbol{\kappa};j;\omega)e^{\beta\omega}\,, \tag{5.7}$$

then the right-hand side of Eq. (5.6) vanishes automatically. In this case, Eq. (5.6) is immediately reduced to the Boltzmann equation for the phonon-distribution function without collision terms.

(5) Taking the limit of $T\to+\infty$, we make use of the identity

$$\lim_{T\to+\infty}\int_0^{T-t_0}d\tau e_{\mp}{}^{i(\omega_1-\omega_2+\omega_3)\tau}\quad\frac{\mp i}{\omega_1-\omega_2+\omega_3\mp i\epsilon}=\mp i\left\{\frac{1}{(\omega_1-\omega_2+\omega_3)_P}\pm i\pi\delta(\omega_1-\omega_2+\omega_3)\right\}, \tag{5.8}$$

where the suffix P is to denote taking the principal value.

(6) Expand $[\omega(\mathbf{p}+\frac{1}{2}\boldsymbol{\kappa}, j_1)-\omega(\mathbf{p}-\frac{1}{2}\boldsymbol{\kappa}, j_1)]$ with respect to $\boldsymbol{\kappa}$, and keep the first term of the expansion. Then, we obtain

$$\omega(\mathbf{p}+\tfrac{1}{2}\boldsymbol{\kappa}, j_1)-\omega(\mathbf{p}-\tfrac{1}{2}\boldsymbol{\kappa}, j_1)=\boldsymbol{\kappa}\cdot\mathbf{v}_{\mathbf{p},j_1}, \qquad (5.9)$$

where

$$\mathbf{v}_{\mathbf{p},j_1}\equiv(\partial\omega(p',j_1)/\partial\mathbf{p}')_{\mathbf{p}'=\mathbf{p}}. \qquad (5.10)$$

$\mathbf{v}_{\mathbf{p},j_1}$ is the group velocity of phonon $(\mathbf{p},j_1)$. This approximation is valid when

$$\boldsymbol{\kappa}\cdot\mathbf{v}_{\mathbf{p},j_1}<\omega(\mathbf{p},j_1). \qquad (5.11)$$

Substituting Eq. (5.9) into the left-hand side of Eq. (5.6), and making use of Eq. (4.3), we can transform the left-hand side of Eq. (5.6) into

$$\mathbf{v}_{\mathbf{p},j_1}\cdot\nabla_{\mathbf{R}}N(\mathbf{p},j_1;\mathbf{R}), \qquad (5.12)$$

which is the usual transport term.

Likewise, we may also expand of the right-hand side of Eq. (5.6), except $\Delta D^{>,<}$, with respect to $\boldsymbol{\kappa}$, and retain terms up to the first order in $(\boldsymbol{\kappa}\cdot\mathbf{v}_{\mathbf{p},j}/\omega(\mathbf{p},j))$.

We notice that $\Delta G^{>}$ and $\Delta D^{>,<}$ are of the same order of magnitude in the lowest order of $(\boldsymbol{\kappa}\cdot\mathbf{v}_{\mathbf{p},j}/\omega(\mathbf{p},j))$, as is seen later. It is also noted that in terms of phonon distribution function, the condition (5.11) can be written as

$$\mathbf{v}_{\mathbf{p},j_1}\cdot\nabla_{\mathbf{R}}N(\mathbf{p},j_1;\mathbf{R})<\omega(\mathbf{p},j_1)N(\mathbf{p},j_1;\mathbf{R}). \qquad (5.13)$$

Therefore, the present approximation is equivalent to neglecting the second and higher order space-derivatives of $N(\mathbf{p},j;\mathbf{R})$, corresponding to the assumption that the spatial variation of $N(\mathbf{p},j;\mathbf{R})$ is slow.

(7) Introduce the spectral density $A(\mathbf{p},j,\omega)$ by

$$D_{\mathrm{eq}}^{>}(\mathbf{p},j,\omega)=i[n(\omega)+1]A(\mathbf{p},j,\omega), \qquad (5.14\mathrm{a})$$

$$D_{\mathrm{eq}}^{<}(\mathbf{p},j,\omega)=in(\omega)A(\mathbf{p},j,\omega), \qquad (5.14\mathrm{b})$$

where

$$n(\omega)=1/(e^{\beta\omega}-1). \qquad (5.15)$$

Then, $A(\mathbf{p},j,\omega)$ can be expressed by

$$A(\mathbf{p},j,\omega)=-i\{D_{\mathrm{eq}}^{>}(\mathbf{p},j,\omega)-D_{\mathrm{eq}}^{<}(\mathbf{p},j,\omega)\}$$
$$=-\int_{-\infty}^{\infty}dt\, e^{i\omega t}\langle[A_{\mathbf{p},j}^{+}(t),A_{\mathbf{p},j}]\rangle_{\mathrm{eq}}. \qquad (5.16)$$

As for the nonequilibrium Green's functions $D^{>,<}$, we put them in the following form:

$$D^{>}(\mathbf{p},\boldsymbol{\kappa},j;\omega)=i[\nu(\mathbf{p},\boldsymbol{\kappa},j;\omega)+1]A(\mathbf{p},j;\omega), \qquad (5.17\mathrm{a})$$

$$D^{<}(\mathbf{p},\boldsymbol{\kappa},j;\omega)=i\nu(\mathbf{p},\boldsymbol{\kappa},j;\omega)A(\mathbf{p},j;\omega), \qquad (5.17\mathrm{b})$$

where we use the same spectral density $A(\mathbf{p},j,\omega)$ as (5.16) and introduce the function ν. Then it follows that

$$\Delta D^{>}(\mathbf{p},\boldsymbol{\kappa},j;\omega)=\Delta D^{<}(\mathbf{p},\boldsymbol{\kappa},j;\omega)$$
$$=i\Delta\nu(\mathbf{p},\boldsymbol{\kappa},j;\omega)A(\mathbf{p},j;\omega), \qquad (5.18)$$

where

$$\Delta\nu(\mathbf{p},\boldsymbol{\kappa},j;\omega)\equiv\nu(\mathbf{p},\boldsymbol{\kappa},j;\omega)-n(\omega). \qquad (5.19)$$

We now transform Eq. (5.6) into the equation for the phonon distribution function. For this purpose, use is made of the relation (4.4) which can be reduced into

$$\Delta G^{>}(\mathbf{p},\boldsymbol{\kappa},j;\omega)$$
$$=[i/2\omega(\mathbf{p},j)]\{\omega-\omega(\mathbf{p},j)\}^2\Delta D^{>}(\mathbf{p},\boldsymbol{\kappa};j;\omega)$$
$$+0((\boldsymbol{\kappa}\cdot\mathbf{k}_{\mathbf{p},j}/\omega(\mathbf{p},j)). \qquad (5.20)$$

We see that $\Delta G^{>}$ and $\Delta D^{>}$ are of the same order of magnitude in the lowest order of $((\boldsymbol{\kappa}\cdot v_{\mathbf{p},j}/\omega(\mathbf{p},j))$, so that we can neglect the second term on the right-hand side of Eq. (5.20).

Substitution of this relation (5.20) and Eq. (5.18) into Eq. (4.3) yields

$$N(\mathbf{p},j;\mathbf{R})-N_{\mathrm{eq}}(\mathbf{p},j)$$
$$=\sum_{\kappa}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-i\kappa\cdot\mathbf{R}}\Delta G^{>}(\mathbf{p},\boldsymbol{\kappa},j;\omega)$$
$$=(-1)\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{\{\omega-\omega(\mathbf{p},j)\}^2}{2\omega(\mathbf{p},j)}A(\mathbf{p},j;\omega)$$
$$\times\Delta\nu(\mathbf{p},j;\mathbf{R};\omega), \qquad (5.21)$$

where

$$\Delta\nu(\mathbf{p},j;\mathbf{R};\omega)=\sum_{\kappa}e^{-i\kappa\cdot\mathbf{R}}\Delta\nu(\mathbf{p},\boldsymbol{\kappa},j;\omega). \qquad (5.22)$$

Thus, we can transform Eq. (5.6) into the equation for $N(\mathbf{p},j,\mathbf{R})$, which is not written down here explicitly, because it is too complicated.

(8) In order to simplify the equation thus obtained, we will make an additional approximation. We take the simplest form for the spectral density:

$$A(\mathbf{p},j;\omega)=(\pi/\omega(\mathbf{p},j))$$
$$\times\{\delta(\omega+\omega(\mathbf{p},j))-\delta(\omega-\omega(\mathbf{p},j))\}. \qquad (5.23)$$

This approximation is valid in the limit of weak interaction, and allowed when the phonon lifetime $\tau(\mathbf{p},j)$ is long enough to satisfy

$$\omega(\mathbf{p},j)\tau(\mathbf{p},j)\gg 1. \qquad (5.24)$$

In this approximation, Eq. (5.21) is reduced to

$$N(\mathbf{p},j;\mathbf{R})-N_{\mathrm{eq}}(\mathbf{p},j)=-\Delta\nu(\mathbf{p},j;\mathbf{R};-\omega(\mathbf{p},j)). \qquad (5.25)$$

Thus, $\Delta\nu$ is directly related to the deviation of phonon distribution function from the equilibrium distribution function. Therefore, in accordance with the argument of Peierls,[1] we introduce a new function g by

$$(-1)\Delta\nu(\mathbf{p},j;\mathbf{R};\omega)=g(\mathbf{p},j;\mathbf{R};\omega)n(\omega)[n(\omega)+1]. \qquad (5.26)$$

It should be noted that this function g satisfies

$$g(\mathbf{p},j;\mathbf{R};\omega)=-g(-\mathbf{p};j;\mathbf{R};-\omega). \qquad (5.27)$$

The proof of this relation is given as follows; if we use the property of operator A_p, Eq. (2.3a), it follows from Eq. (5.16) that

$$A(\mathbf{p},j;\omega)=-A(-\mathbf{p},j;-\omega). \qquad (5.28)$$

Similarly, it also follows from Eq. (2.7) that

$$\Delta D^{>}(-\mathbf{p},\boldsymbol{\kappa},j;-\omega)=\Delta D^{<}(\mathbf{p},\boldsymbol{\kappa},j;\omega). \tag{5.29}$$

On the other hand, it is obvious from Eq. (5.15) that

$$n(-\omega)=-[n(\omega)+1]. \tag{5.30}$$

Substituting Eqs. (5.26), (5.28), and (5.29) into Eq. (5.18), and making use of Eq. (5.30), we obtain the relation (5.27).

By making use of Eq. (5.27), we obtain finally the Boltzmann equation for N, which is given by

$$\begin{aligned}
&\mathbf{v}_{\mathbf{p},j}\cdot\nabla_{\mathbf{R}}N(\mathbf{p},j;\mathbf{R})\\
&=\sum_{\mathbf{p}',\mathbf{p}''}\sum_{j',j''}\frac{\pi}{2\omega_{\mathbf{p},j}\omega_{\mathbf{p}',j'}\omega_{\mathbf{p}'',j''}}\{|V(\mathbf{p},j;-\mathbf{p}',j';\mathbf{p}'',j'')|^2\delta(\omega_{\mathbf{p},j}-\omega_{\mathbf{p}',j'}+\omega_{\mathbf{p}'',j''})[n_{\mathbf{p},j}+1]n_{\mathbf{p}',j'}[n_{\mathbf{p}'',j''}+1]\\
&\quad\times[-g(\mathbf{p},j;\mathbf{R};-\omega_{\mathbf{p},j})+g(\mathbf{p}',j';\mathbf{R};-\omega_{\mathbf{p}',j'})-g(\mathbf{p}'',j'';\mathbf{R};-\omega_{\mathbf{p}'',j''})]\\
&\quad+\tfrac{1}{2}|V(\mathbf{p},j;-\mathbf{p}',j';-\mathbf{p}'',j'')|^2\delta(\omega_{\mathbf{p},j}-\omega_{\mathbf{p}',j'}-\omega_{\mathbf{p}'',j''})\\
&\quad\times[n_{\mathbf{p},j}+1]n_{\mathbf{p}',j'}n_{\mathbf{p}'',j''}[-g(\mathbf{p},j;\mathbf{R};-\omega_{\mathbf{p}'j})+g(\mathbf{p}',j';\mathbf{R};-\omega_{\mathbf{p}',j'})+g(\mathbf{p}'',j'';\mathbf{R};-\omega_{\mathbf{p}'',j''})]\}\\
&\quad-\alpha(\mathbf{p},j)\mathbf{v}_{\mathbf{p},j}\cdot\nabla_{\mathbf{R}}N(\mathbf{p},j;\mathbf{R})+\sum_{\mathbf{p}',j'}\{\beta^{(1)}(\mathbf{p},j;\mathbf{p}',j')\mathbf{v}_{\mathbf{p},j}+\beta^{(2)}(\mathbf{p},j;\mathbf{p}',j')\mathbf{v}_{\mathbf{p}',j'}\}\cdot\nabla_{\mathbf{R}}N(\mathbf{p}',j';\mathbf{R})\\
&\quad-\sum_{\mathbf{p}'',j''}\{\gamma^{(1)}(\mathbf{p},j;\mathbf{p}'',j'')\mathbf{v}_{\mathbf{p},j}+\gamma^{(2)}(\mathbf{p},j;\mathbf{p}'',j'')\mathbf{v}_{\mathbf{p}'',j''}\}\cdot\nabla_{\mathbf{R}}N(\mathbf{p}'',j'';\mathbf{R}).
\end{aligned} \tag{5.31}$$

In this equation we have used the abbreviation that

$$n_{\mathbf{p},j}=1/(e^{\beta\omega_{\mathbf{p},j}}-1), \tag{5.32}$$

$$\begin{aligned}
\alpha(\mathbf{p},j)=&\sum_{\mathbf{p}',\mathbf{p}''}\sum_{j',j''}\{8\omega_{\mathbf{p},j}^2\omega_{\mathbf{p}',j'}\omega_{\mathbf{p}'',j''}\}^{-1}[n_{\mathbf{p},j}+1]^{-1}\\
&\times\left\{\frac{n_{\mathbf{p}',j'}[n_{\mathbf{p}'',j''}+1]}{(\omega_{\mathbf{p}'j}-\omega_{\mathbf{p}',j'}+\omega_{\mathbf{p}'',j''})_P}+\frac{1}{2}\frac{[n_{\mathbf{p}',j'}+1][n_{\mathbf{p}'',j''}+1]}{(\omega_{\mathbf{p},j}+\omega_{\mathbf{p}',j'}+\omega_{\mathbf{p}'',j''})_P}+\frac{1}{2}\frac{n_{\mathbf{p}',j'}n_{\mathbf{p}'',j''}}{(\omega_{\mathbf{p},j}-\omega_{\mathbf{p}',j'}-\omega_{\mathbf{p}'',j''})_P}\right\}\\
&\times\left\{|V(\mathbf{p},j;-\mathbf{p}',j';\mathbf{p}'',j'')|^2-\frac{2\omega_{\mathbf{p},j}}{v_{\mathbf{p},j}}\left(\frac{\mathbf{v}_{\mathbf{p},j}}{v_{\mathbf{p},j}}\cdot\frac{\partial}{\partial\mathbf{p}}|V(\mathbf{p},j;-\mathbf{p}',j';\mathbf{p}'',j'')|^2\right)\right\},
\end{aligned} \tag{5.33}$$

$$\begin{aligned}
\beta^{(1)}(\mathbf{p},j;\mathbf{p}',j')=&\sum_{\mathbf{p}'',j''}\{4\omega_{\mathbf{p},j}\omega_{\mathbf{p}',j'}\omega_{\mathbf{p}'',j''}\}^{-1}[n_{\mathbf{p}',j'}+1]^{-1}n_{\mathbf{p}',j'}^{-1}n_{\mathbf{p},j}|V(\mathbf{p},j;-\mathbf{p}',j';\mathbf{p}'',j'')|^2\\
&\times\left\{\frac{[n_{\mathbf{p}',j'}+1]n_{\mathbf{p}'',j''}}{(\omega_{\mathbf{p},j}-\omega_{\mathbf{p}',j'}+\omega_{\mathbf{p}'',j''})_P{}^2}+\frac{1}{2}\frac{[n_{\mathbf{p}',j'}+1][n_{\mathbf{p}'',j''}+1]}{(\omega_{\mathbf{p},j}-\omega_{\mathbf{p}',j'}-\omega_{\mathbf{p}'',j''})_P{}^2}-\frac{1}{2}\frac{n_{\mathbf{p}',j'}n_{\mathbf{p}'',j''}}{(\omega_{\mathbf{p},j}+\omega_{\mathbf{p}',j'}+\omega_{\mathbf{p}'',j''})_P{}^2}\right\}\\
&+\sum_{p'',j''}\{2\omega_{\mathbf{p},j}\omega_{\mathbf{p}',j'}\omega_{\mathbf{p}'',j''}\}^{-1}n_{\mathbf{p}j}\left\{\delta(\omega_{\mathbf{p},j}-\omega_{\mathbf{p}',j'}+\omega_{\mathbf{p}'',j''})+\frac{1}{2}\frac{[n_{\mathbf{p}'',j''}+1]}{n_{\mathbf{p}'',j''}}\delta(\omega_{\mathbf{p},j}-\omega_{\mathbf{p}',j'}-\omega_{\mathbf{p}'',j''})\right\}\\
&\times\frac{\pi}{v_{\mathbf{p},j}}\operatorname{Im}\left\{\left[\frac{\mathbf{v}_{\mathbf{p},j}}{v_{\mathbf{p},j}}\cdot\frac{\partial}{\partial\mathbf{p}}V(\mathbf{p},j;-\mathbf{p}',j';p'',j'')\right]V^*(\mathbf{p},j;-\mathbf{p}',j';\mathbf{p}'',j'')\right\},
\end{aligned} \tag{5.34}$$

$$\begin{aligned}
\beta^{(2)}(\mathbf{p},j;\mathbf{p}',j')=&\sum_{\mathbf{p}'',j''}\operatorname{Im}\left\{\left[\frac{\mathbf{v}_{\mathbf{p}',j'}}{v_{\mathbf{p}',j'}}\cdot\frac{\partial}{\partial\mathbf{p}'}V(\mathbf{p},j;-\mathbf{p}',j';\mathbf{p}'',j'')\right]V^*(\mathbf{p},j;-\mathbf{p}',j';\mathbf{p}'',j'')\right\}\frac{1}{v_{\mathbf{p}',j'}}\\
&\times\{2\omega_{\mathbf{p},j}\omega_{\mathbf{p}',j'}\omega_{\mathbf{p}'',j''}\}^{-1}\pi n_{\mathbf{p},j}\left\{\delta(\omega_{\mathbf{p},j}-\omega_{\mathbf{p}',j'}+\omega_{\mathbf{p}'',j''})+\frac{1}{2}\frac{[n_{\mathbf{p}'',j''}+1]}{n_{\mathbf{p}'',j''}}\delta(\omega_{\mathbf{p},j}-\omega_{\mathbf{p}',j'}-\omega_{\mathbf{p}'',j''})\right\},
\end{aligned} \tag{5.35}$$

$$\gamma^{(1)}(\mathbf{p},j;\mathbf{p}'',j'')=\sum_{\mathbf{p}',j'}\{4\omega_{\mathbf{p},j}\omega_{\mathbf{p}',j'}\omega_{\mathbf{p}'',j''}\}^{-1}\{n_{\mathbf{p}'',j''}[n_{\mathbf{p}'',j''}+1]\}^{-1}n_{\mathbf{p},j}|V(\mathbf{p},j;-\mathbf{p}',j';\mathbf{p}'',j'')|^2$$
$$\times\left\{\frac{[n_{\mathbf{p}',j'}+1]n_{\mathbf{p}'',j''}}{(\omega_{\mathbf{p},j}-\omega_{\mathbf{p}',j'}+\omega_{\mathbf{p}'',j''})_P{}^2}-\frac{1}{2}\frac{[n_{\mathbf{p}',j'}+1][n_{\mathbf{p}'',j''}+1]}{(\omega_{\mathbf{p},j}-\omega_{\mathbf{p}',j'}-\omega_{\mathbf{p}'',j''})_P{}^2}+\frac{1}{2}\frac{n_{\mathbf{p}',j'}n_{\mathbf{p}'',j''}}{(\omega_{\mathbf{p},j}+\omega_{\mathbf{p}',j'}+\omega_{\mathbf{p}'',j''})_P{}^2}\right\}$$
$$+\sum_{\mathbf{p}',j'}\{2\omega_{\mathbf{p},j}\omega_{\mathbf{p}',j'}\omega_{\mathbf{p}'',j''}\}^{-1}[n_{\mathbf{p}'',j''}+1]^{-1}n_{\mathbf{p},j}[n_{\mathbf{p}',j'}+1]$$
$$\times\left\{\delta(\omega_{\mathbf{p},j}-\omega_{\mathbf{p}',j'}+\omega_{\mathbf{p}'',j''})-\frac{1}{2}\frac{[n_{\mathbf{p}'',j''}+1]}{n_{\mathbf{p}'',j''}}\delta(\omega_{\mathbf{p},j}-\omega_{\mathbf{p}',j'}-\omega_{\mathbf{p}'',j''})\right\}$$
$$\times\frac{\pi}{v_{\mathbf{p},j}}\operatorname{Im}\left\{\left[\frac{\mathbf{v}_{\mathbf{p},j}}{v_{\mathbf{p},j}}\cdot\frac{\partial}{\partial\mathbf{p}}V(\mathbf{p},j;-\mathbf{p}',j';\mathbf{p}'',j'')\right]V^*(\mathbf{p},j;-\mathbf{p}',j';\mathbf{p}'',j'')\right\},\quad(5.36)$$

$$\gamma^{(2)}(\mathbf{p},j;\mathbf{p}'',j'')=\sum_{\mathbf{p}',j'}(-1)\pi\{2\omega_{\mathbf{p},j}\omega_{\mathbf{p}',j'}\omega_{\mathbf{p}'',j''}\}^{-1}[n_{\mathbf{p}'',j''}+1]^{-1}n_{\mathbf{p},j}[n_{\mathbf{p}',j'}+1]$$
$$\times\left\{\delta(\omega_{\mathbf{p},j}-\omega_{\mathbf{p}',j'}+\omega_{\mathbf{p}'',j''})-\frac{1}{2}\frac{[n_{\mathbf{p}'',j''}+1]}{n_{\mathbf{p}'',j''}}\delta(\omega_{\mathbf{p},j}-\omega_{\mathbf{p}',j'}-\omega_{\mathbf{p}'',j''})\right\}$$
$$\times\frac{1}{v_{\mathbf{p}'',j''}}\operatorname{Im}\left\{\left[\frac{\mathbf{v}_{\mathbf{p}'',j''}}{v_{\mathbf{p}'',j''}}\cdot\frac{\partial}{\partial\mathbf{p}''}V(\mathbf{p},j;-\mathbf{p}',j';p'',j'')\right]V^*(\mathbf{p},j;-\mathbf{p}',j';\mathbf{p}'',j'')\right\}.\quad(5.37)$$

If we compare Eq. (5.31) with Peierls' integral equation for phonon distribution [Eq. (2.76) of his book[1]], we see that the terms represented by the first four lines on the right-hand side of Eq. (5.31) are identical with the collision term of Peierls' equation. Equation (5.31) includes the additional terms represented by the last three lines on the right-hand side, which were omitted in the Peierls' equation. These additional terms as well as the transport term on the left-hand side of Eq. (5.31) arise because the wave packets have a small spread in wave vectors around the mean wave vector.

One of the additional terms, which is represented by $-\alpha(\mathbf{p},j)\mathbf{v}_{\mathbf{p},j}\cdot\nabla_{\mathbf{R}}N(\mathbf{p},j;\mathbf{R})$, can be transferred to the left-hand side of Eq. (5.31) to modify the original transport term. In addition, if the spatial variation of $N(\mathbf{p},j;\mathbf{R})$ satisfies a simple relation such that

$$\nabla_{\mathbf{R}}N(\mathbf{p}',j';\mathbf{R})=C(\mathbf{p}',j';\mathbf{p},j)\nabla_{\mathbf{R}}N(\mathbf{p},j;\mathbf{R}),\quad(5.38)$$

then the terms represented by the last two lines on the right-hand side of Eq. (5.31) also can be rearranged so as to modify the transport term on the left of Eq. (5.31). Obviously, such a modification of the transport term results in the replacement of the phonon group velocity $\mathbf{v}_{\mathbf{p},j}$ by the new velocity, which will be just a renormalized phonon group velocity.

It is interesting to observe that the relation (5.38) is not unreasonable. In fact, according to Peierls, we put

$$N(\mathbf{p},j;\mathbf{R})=n_{\mathbf{p},j}+N^1(\mathbf{p},j;\mathbf{R}),\quad(5.39)$$

and assume that $n_{\mathbf{p},j}$ shows $\mathbf{R}$ dependence only through the temperature factor $T(\mathbf{R})$ (introduction of the idea of local temperature), then $\nabla_{\mathbf{R}}N(\mathbf{p},j;\mathbf{R})$ can be replaced by

$$\nabla_{\mathbf{R}}N(\mathbf{p},j;\mathbf{R})=\frac{\partial n_{\mathbf{p},j}(T)}{\partial T}\nabla_{\mathbf{R}}T=n_{\mathbf{p},j}[n_{\mathbf{p},j}+1]\frac{\omega_{\mathbf{p},j}}{kT^2}\nabla_{\mathbf{R}}T,\quad(5.40)$$

because we can neglect N^1 in the transport term, as was discussed by Peierls.[1] In this case, we have the simple relation

$$\nabla_{\mathbf{R}}N(\mathbf{p}',j';\mathbf{R})=\frac{n_{\mathbf{p}',j'}[n_{\mathbf{p}'j'}+1]}{n_{\mathbf{p},j}[n_{\mathbf{p},j}+1]}\frac{\omega_{\mathbf{p}',j'}}{\omega_{\mathbf{p},j}}\nabla_{\mathbf{R}}N(\mathbf{p},j;\mathbf{R}).\quad(5.41)$$

VI. DISCUSSION

In summary, we have presented in this paper a Green's function approach to derive the Boltzmann equation for the phonon distribution function in an interacting pure-phonon system. The Boltzmann equation derived is identical with the Peierls integral equation, except for certain additional correction terms. Under a reasonable condition [see Eq. (5.38)], the correction terms can be absoibed into the transport term, provided that the phonon group velocity appearing in the original transport terms is replaced by the renormalized one. Tracing the procedure of deriving the Boltzmann equation, we can find that the renormalizing effect of the phonon-group velocity is related not only to collisions of three wave packets of phonons, but also to interactions between phonons constituting the wave packet itself.

One may suppose that the renormalization of the phonon group velocity should come partly from the shift of the phonon spectrum due to interactions. It is hard to identify this effect in our expressions (5.33)–(5.37). However, it is rather obvious that in the expression of the renormalized group velocity there is also included another effect, which is connected with the wave vector spread in the representation of the wave packets. It is possible that we could estimate the contribution due to the usual phonon-energy shift, if we take the expression of the renormalized phonon frequency, which is given by Maradudin and Fein.[4] No further discussion of this matter is given here.

In the present derivation of the Boltzmann equation, we eventually assumed that the t_0 dependence of the nonequilibrium Green's functions can be neglected. If this t_0-dependence were not neglected, it would yield additional terms to the Boltzmann equation. Formally, it seems that the analytic and asymptotic conditions imposed are sufficient to have a well defined problem. However, the expression of the Fourier transform of the Boltzmann equation corresponding to (5.6) would contain not only a term in Ω, a transform variable conjugate to t_0, and representing $(\partial/\partial t_0)$ on the left-hand side, but also there would be a complicated modification of the collision terms due to conservation conditions which now must incorporate Ω. Since the t_0 dependence of the phonon distribution function provides an additional energy to the system, the conservation of energy of wave packets in collisions should be modified. For example, we can see that the factor $\delta(\omega_{\mathbf{p},j}-\omega_{\mathbf{p}',j'}+\omega_{\mathbf{p}'',j''})$, which appears in Eq. (5.31) should be replaced by

$$\tfrac{1}{2}\delta(\omega_{\mathbf{p},j}-\omega_{\mathbf{p}',j'}+\omega_{\mathbf{p}'',j''}+\tfrac{1}{2}\Omega)+\tfrac{1}{2}\delta(\omega_{\mathbf{p},j}-\omega_{\mathbf{p}',j'}+\omega_{\mathbf{p}'',j''}-\tfrac{1}{2}\Omega),$$

where Ω represents the frequency corresponding to the t_0 dependence. The direction in which further approximations to cover the cases where either the distribution or the collision terms must be corrected because of a rapid dependence on t_0 is indicated by the present approach, but is yet to be worked out in detail.

Since we have seen that the Boltzmann equation of the Peierls type is still valid within the framework of the lowest-order scattering process, we can refer questions of its solution to standard references. Here we are content to note that the solution $g(\mathbf{p},j;\mathbf{R};-\omega_{\mathbf{p},j})$ should satisfy the symmetry property represented by Eq. (5.27).

Finally, we wish to make a few remarks on the generalization of the Boltzmann equation. It seems possible to include the effect of the finite lifetime of phonons into the Boltzmann equation if we use a more general expression of the spectral density $A(\mathbf{p},j;\omega)$ instead of using Eq. (5.23), in the step (8) mentioned in Sec. V. (We do not discuss the result here.) It also seems interesting to generalize the Boltzmann equation to include higher order scattering processes. However, there is no guarantee, for example, that the higher-order scattering processes via cubic interaction are as important as the lower-order scattering processes by quartic interactions. Even if this were true, it would not be sufficient to replace the cubic interaction matrix $V(k_1,k_2,k_3)$ appearing in the Peierls equation by a more general T matrix, which could be obtained from the perturbation series for V. Obviously, we should also take into account the possibility that the phonon Green's functions constituting the T matrix should be replaced by the nonequilibrium ones, so that they would yield additional terms to the Peierls equation.

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APPENDIX

We derive Eq. (3.4), in which the Green's function R is expressed in terms of D. The function R defined by Eq. (3.3) can be expressed in terms of functional derivatives[6] with respect to $J_k(t)$ as follows:

$$R(-k_2,t_1;k_3,t_1;p_2,t_2)=\frac{1}{i}\frac{1}{\langle S\rangle}\frac{\delta\{\langle S\rangle D(-k_3,t_1;p_2,t_2)\}}{\delta J_{-k}1(t_1)}=\frac{1}{i}\frac{\delta\ln\langle S\rangle}{\delta J_{-k_2}(t_1)}D(-k_3,t_1;p_2,t_2)+\frac{1}{i}\frac{\delta D(-k_3,t_1;p_2,t_2)}{\delta J_{-k_2}(t_1)}. \quad (A.1)$$

From the definition of S, we obtain

$$\frac{1}{i}\frac{\delta\ln\langle S\rangle}{\delta J_{-k_2}(t_1)}=\frac{1}{\langle S\rangle}\langle T\{A_{-k_2}(t_1)S\}\rangle=\bar{A}_{-k_2}(t_1). \quad (A.2)$$

It is also seen that

$$-\delta\bar{A}_p(t)/\delta J_{p'}(t')=D(-p,t;p',t')+i\bar{A}_p(t)\bar{A}_{p'}(t'), \quad (A.3)$$

so that $\bar{A}_p(t)$ can be regarded as representing the phonon field generated by the creation of phonons, p' at time t'. From (A.3), we can regard $D(-p,t;p',t')$ as being a functional of $\bar{A}$. Thus, we have

$$\frac{1}{i}\frac{\delta D(-k_3,t_1;p_2,t_2)}{\delta J_{-k_2}(t_1)}=\frac{1}{i}\sum_{q_2}\int_{t_0}^{t_0-i\beta}d\tau_2\frac{\delta D(-k_3,t_1;p_2,t_2)}{\delta\bar{A}_{p_2}(\tau_2)}\frac{\delta\bar{A}_{q_2}(\tau_2)}{\delta J_{-k_2}(t_1)}. \quad (A.4)$$

[6] V. L. Bonch-Bruevich and S. V. Tyabloikv, *The Green Function Method in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1962).

On the other hand, we introduce the inverse of the phonon Green's function by

$$\sum_{p''}\int_{t_0}^{t_0-i\beta} dt'' D(p,t;p'',t'')D^{-1}(p'',t'';p',t')=\delta(it-it')\delta(p-p'). \tag{A.5}$$

Taking the functional derivatives of both sides of this equation with respect to $\bar{A}_q(\tau)$, and using (A.5) again, we obtain

$$\frac{\delta D(-k_3,t_1;p_2,t_2)}{\delta\bar{A}_{p_2}(\tau_2)}=(-1)\sum_{q_1,q_3}\int_{t_0}^{t_0-i\beta}d\tau_1\int_{t_0}^{t_0-i\beta}d\tau_3 D(-k_3,t_1;-q_3,\tau_3)\frac{\delta D^{-1}(-q_3,\tau_3;q_1,\tau_1)}{\delta\bar{A}_{p_2}(\tau_2)}D(q_1,\tau_1;p_2,t_2)$$
$$=\sum_{q_1,q_3}\int_{t_0}^{t_0-i\beta}d\tau_1\int_{t_0}^{t_0-i\beta}d\tau_3\Gamma(-q_3,\tau_3;q_2,\tau_2;-q_1,\tau_1)D(-k_3,t_1;-q_3,\tau_3)D(q_1,\tau_1;p_2,t_2), \tag{A.6}$$

where we used the notation Γ (see Eq. (3.6)]. If we use (A.3) and (A.6) into (A.4), and then (A.4) thus obtained and (A.2) into (A.1), we obtain

$$R(-k_2,t_1;k_3,t_1;p_2,t_2)$$
$$=\sum_{q_1}\int_{t_0}^{t_0-i\beta}d\tau_1\Big\{A_{-k_2}(t_1)\delta(q_1+k_3)\delta(i\tau_1-it_1)+i\sum_{q_2,q_3}\int_{t_0}^{t_0-i\beta}d\tau_2\int_{t_0}^{t_0-i\beta}d\tau_3\Gamma(-q_3,\tau_3;q_2,\tau_2;-q_1,\tau_1)D(q_3,\tau_3;k_3,t_1)$$
$$\times D(q_1,\tau_1;p_2,t_2)[D(k_2,t_1;q_2\tau_2)+i\bar{A}_{q_2}(\tau_2)\bar{A}_{-k_2}(t_1)]\Big\}, \tag{A.7}$$

where we have used the property

$$D(p,t;p',t')=D(-p',t';-p,t), \tag{A.8}$$

which is obvious from Eq. (2.3a) and the definition of D, Eqs. (2.6) and (2.7). Substitution of (A.7) into Eq. (3.2a) yields Eq. (3.4).

The last equality of Eq. (3.6) comes from the following consideration. Suppose $D(p_1,t_1;p_2,t_2)$ are matrix elements of a matrix D. Then, Eq. (3.4) can be written in a matrix form

$$D=D_0-D_0LD. \tag{A.9}$$

Then, it easily follows that

$$L=D^{-1}-D_0^{-1}. \tag{A.10}$$

Thus, we are led to the last equation of Eq. (3.6), because D_0^{-1} is independent of $\bar{A}$.

Finally, we calculate the vertex Γ [Eq. (3.6)] in the lowest approximation, in which we take the first term of Eq. (3.5) for L. Then, we use the Γ obtained into the second term on the right-hand side of Eq. (3.5) and neglect terms including $\bar{A}(t)$ explicitly. The result is given by

$$L(p_1,t_1;q,\tau)=\frac{1}{i}\sum_{k_2,k_3}\sum_{q_2,q_3}V(p_1,-k_2,k_3)V(-q,q_2,-q_3)D(k_2,t_1;q_2,\tau)D(q_3,\tau;k_3,t_1). \tag{A.11}$$

Substituting this into Eq. (3.4), we obtain the term represented by the diagram (a) in Fig. 1.