Energy-Flux Operator for a Lattice*†

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(Received 31 May 1963)

A systematic derivation of the energy-flux operator for a three-dimensional lattice is given. The treatment is based on the general expressions for the energy flux which are valid for all phases of matter; a short derivation of these expressions, making no restrictions to two-body forces, is presented. The average energy flux is transformed to the phonon representation, and it is shown that the diagonal contribution from the harmonic forces has the familiar form $\sum_{\mathbf{k}s} N_{\mathbf{k}s}\hbar\omega_{\mathbf{k}s}\mathbf{v}_{\mathbf{k}s}$. There are, in addition, nondiagonal contributions to the energy flux, even in the harmonic approximation. The significance of these corrections is discussed. The contributions to the average flux from the anharmonic forces and from lattice imperfections are also treated. Finally, the problem of forming wave packets of the plane-wave normal modes to obtain an expression for the local energy flux is considered.

1. INTRODUCTION

THE theory for the lattice contribution to the thermal conductivity of solids is usually based on the Boltzmann equation for phonons.[1–3] In this theory, which was first presented by Peierls,[4] and also in the more modern approach utilizing correlation functions,[5,6] it is necessary to know the functional dependence of the energy-flux operator[7] on the dynamical variables of the system. For a lattice these are the creation and annihilation operators for phonons. The form usually used for the flux in a lattice is[1–3]

$$\mathbf{S}=V^{-1}\sum_{\mathbf{k}s} N_{\mathbf{k}s}\hbar\omega_{\mathbf{k}s}\mathbf{v}_{\mathbf{k}s}, \tag{1.1}$$

where $N_{\mathbf{k}s}$, $\omega_{\mathbf{k}s}$ and $\mathbf{v}_{\mathbf{k}s}$ are, respectively, the number operator, frequency, and group velocity of the plane-wave normal mode with wave vector $\mathbf{k}$ and polarization index s, and V is the volume of the system. This result was obtained by Peierls[4] who considered in detail a linear chain with nearest neighbor interactions and then generalized to three dimensions. The validity of (1.1) is generally accepted, although no rigorous derivation of it has been given for the three-dimensional case.

Here a systematic derivation of the energy-flux operator for three-dimensional lattices is given, and the limitations of, and corrections to, (1.1) are discussed. The treatment is based on the general expressions which give the energy flux in terms of the particle variables and which are valid for all phases of matter.[6,8,9] For completness a derivation of these formulas, making no restriction to two-body forces, is presented in Sec. 2. The results are then transformed to the phonon representation and in Sec. 3 the usual expression (1.1) is obtained as the diagonal part of the harmonic contribution to the average energy flux. Nondiagonal contributions to the flux from the harmonic Hamiltonian are also obtained. In Sec. 4 the contribution to the energy flux from the cubic part of the anharmonic Hamiltonian is calculated, and the effects of lattice imperfections are discussed. The problem of forming wave packets of the plane-wave normal modes in order to describe a local property,[3] in this case the local energy flux, is treated in Sec. 5.

The corrections to expression (1.1) for the energy flux give rise to changes in the formulas determining the thermal conductivity. A discussion of these changes will be given elsewhere.[10]

After completion of this research it was learned that work on the same problem was being carried out by Maradudin,[11] Magid,[12] and Choquard.[13] Their results are less complete than those obtained here, since they do not start from as general a point of view but begin with models limited to a lattice. In particular, they do not obtain the contributions $\mathbf{S}_3^0$ and $\lambda\mathbf{S}_4'$ discussed in Secs. 3 and 4.

* This work was supported by the National Science Foundation.

† Based on part of the author's doctoral dissertation submitted to Lehigh University, June, 1962.

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2. GENERAL EXPRESSIONS FOR THE ENERGY FLUX

The local energy-flux operator $\mathbf{s}(\mathbf{x})$ can be obtained by requiring that it satisfy the equation for energy conservation[14]

$$\dot{H}(\mathbf{x})+\nabla\cdot\mathbf{s}(\mathbf{x})=0, \tag{2.1}$$

where $\dot{H}(\mathbf{x})$ is related to the energy-density operator $H(\mathbf{x})$ and the Hamiltonian of the system H by

$$\dot{H}(\mathbf{x})=(i\hbar)^{-1}[H(\mathbf{x}),H]. \tag{2.2}$$

On combining these expressions one gets

$$\nabla\cdot\mathbf{s}(\mathbf{x})=(i/\hbar)[H(\mathbf{x}),H]. \tag{2.3}$$

In this section the above result is used to obtain the expression giving the energy flux as a function of particle variables.[15]

To proceed further, explicit expressions for the Hamiltonian and energy density are needed; it is desirable that they be defined as generally as possible. Here a Hamiltonian is assumed of the form

$$H=\sum_i\left(\frac{p_i^2}{2m_i}+V_i\right), \tag{2.4}$$

where $\mathbf{p}_i$ is the momentum, m_i is the mass, V_i is the potential energy associated with the ith particle, and the summation is over all the particles in the system. It is assumed that the V_i are functions of the position variables $\mathbf{q}_i$ only; each V_i depends on the position variables for all the particles with which particle i interacts. The separation of the potential energy of the system into the parts V_i is somewhat arbitrary, but a natural choice usually suggests itself in any given problem [see, e.g., (3.18), (4.7), and (4.19)].

When treating the transport properties of a system one uses variables which describe the average properties of small regions containing large numbers of particles. The linear dimensions of these regions will be characterized here by l. It is convenient to reflect this average nature of the macroscopic variables in the choice of the microscopic energy density operator by defining $H(\mathbf{x})$ as

$$H(\mathbf{x})=\tfrac{1}{2}\sum_i\left\{\Delta(\mathbf{x}-\mathbf{q}_i)\left(\frac{p_i^2}{2m_i}+V_i\right)+\text{H.c.}\right\}, \tag{2.5}$$

where the function $\Delta(\mathbf{x}-\mathbf{q}_i)$ is defined to be negligibly small when $|\mathbf{x}-\mathbf{q}_i|>l$ and large but finite when $|\mathbf{x}-\mathbf{q}_i|<l$. (The notation H.c. indicates that the Hermitian conjugate is to be added.) Since the integral of the energy density over the volume of the system must equal the total energy H, it is stipulated that

$$\int dv\,\Delta(\mathbf{x}-\mathbf{q}_i)=1. \tag{2.6}$$

One desires for calculational purposes that the function $\Delta(\mathbf{x}-\mathbf{q}_i)$ be mathematically well behaved; a possible choice is[16]

$$\Delta(\mathbf{x}-\mathbf{q}_i)=\pi^{-3/2}l^{-3}\exp[-|\mathbf{x}-\mathbf{q}_i|^2/l^2]. \tag{2.7}$$

The momentum and position operators $\mathbf{p}_i$ and $\mathbf{q}_i$ obey the commutation relations

$$\begin{aligned}&[q_i^a,p_j^b]=i\hbar\delta^{ab}\delta_{ij}\\ \text{and}\qquad&\\ &[p_i^a,p_j^b]=[q_i^a,q_j^b]=0,\end{aligned} \tag{2.8}$$

where superscripts label vector components, and δ^{ab} and δ_{ij} are Kronecker-δ functions. Using these and the forms for H and $H(\mathbf{x})$ assumed above, one can show that

$$\begin{aligned}\frac{i}{\hbar}[H(\mathbf{x}),H]=-\tfrac{1}{2}\sum_{ij}\Bigg\{\sum_a\Bigg(&\frac{1}{i\hbar}[\Delta(\mathbf{x}-\mathbf{q}_i),p_j^a]\frac{p_j^a}{2m_j}\\&+\frac{p_j^a}{2m_j}\frac{1}{i\hbar}[\Delta(\mathbf{x}-\mathbf{q}_i),p_j^a]\Bigg)\left(\frac{p_i^a}{2m_i}+V_i\right)\\&+(\Delta(\mathbf{x}-\mathbf{q}_i)-\Delta(\mathbf{x}-\mathbf{q}_j))\frac{1}{i\hbar}\left[\frac{p_i^2}{2m_i},V_j\right]\Bigg\}+\text{H.c.}\end{aligned} \tag{2.9}$$

It follows from the commutation relations, e.g., by using the representation where $p_i^a=(\hbar/i)\partial/\partial q_i^a$, that

$$(i/\hbar)[\Delta(\mathbf{x}-\mathbf{q}_i),p_j^a]=\delta_{ij}\partial\Delta(\mathbf{x}-\mathbf{q}_i)/\partial x^a. \tag{2.10}$$

Also, making a Taylor series expansion of $\Delta(\mathbf{x}-\mathbf{q}_i)$, one obtains

$$\begin{aligned}\Delta(\mathbf{x}-\mathbf{q}_j)-\Delta(\mathbf{x}-\mathbf{q}_i)=&\sum_a[\partial(q_i^a-q_j^a)/\partial x^a]\\&\times\Bigg(1+\cdots+\frac{1}{(s+1)!}\sum_{b\cdots r}(q_i^b-q_j^b)\cdots\\&\times(q_i^r-q_j^r)\frac{\partial}{\partial x^b}\cdots\frac{\partial}{\partial x^r}\Bigg)\Delta(\mathbf{x}-\mathbf{q}_i),\end{aligned} \tag{2.11}$$

where there are s summation indices $b\cdots r$. Note that $\partial/\partial x^a$ operates on the function $\Delta(\mathbf{x}-q_i)$ only. The substitution of formulas (2.10) and (2.11) into (2.9) allows one to factor the operator $\partial/\partial x^a$ to the left of the resulting expression, which then has the form

$$(i/\hbar)[H(\mathbf{x}),H]=\sum_a\partial s^a(\mathbf{x})/\partial x^a \tag{2.3}$$

[14] The operator $\dot{H}(\mathbf{x})$ is defined so that $d\langle H(\mathbf{x})\rangle/dt=\langle\dot{H}(\mathbf{x})\rangle$, where $\langle\ \rangle$ indicates an ensemble average. The macroscopic conservation law analogous to (2.1) is $d\langle H(\mathbf{x})\rangle/dt+\nabla\cdot\langle\mathbf{s}(\mathbf{x})\rangle=0$.

[15] The classical analogs of the results obtained in this section can be obtained by replacing $(i/\hbar)[p_i^a,V_j]$ by $\partial V_j/\partial q_i^a$.

[16] M. S. Green [J. Chem. Phys. **22**, 399 (1954)] and H. Mori, I. Oppenheim, and J. Ross (see Ref. 6; p. 281) suggest an alternative choice:

$$\Delta(\mathbf{x}-\mathbf{q}_i)=L^{-3}\sum_{\mathbf{k}}\exp[-i\mathbf{k}\cdot(\mathbf{x}-\mathbf{q}_i)],$$

where k^1, k^2, $k^3\leq 2\pi/l$ and L characterizes the linear dimensions of the system.

with

$$\mathbf{s}(\mathbf{x})=\frac{1}{2}\Big\{\sum_i\Big(\Delta(\mathbf{x}-\mathbf{q}_i)\frac{\mathbf{p}_i}{2m_i}+\frac{\mathbf{p}_i}{2m_i}\Delta(\mathbf{x}-\mathbf{q}_i)\Big)\Big(\frac{p_i^2}{2m_i}+V_i\Big)$$
$$+\sum_{ij}\Big(1+\frac{1}{2!}\sum_b(q_i{}^b-q_j{}^b)\frac{\partial}{\partial x^b}+\cdots\Big)\Delta(\mathbf{x}-\mathbf{q}_i)$$
$$\times(\mathbf{q}_i-\mathbf{q}_j)\frac{1}{i\hbar}\Big[\frac{p_i^2}{2m_i},V_j\Big]\Big\}+\text{H.c.} \quad (2.12)$$

This is the desired expression for the local energy-flux operator.[17] From the above derivation it is apparent that the conservation equation (2.1) is simply a rewriting of Eq. (2.2) for $\dot{H}(\mathbf{x})$.

For determining the thermal conductivity[5] one needs an expression for the average energy flux $\mathbf{S}$ which is defined as

$$\mathbf{S}=V^{-1}\int dv\,\mathbf{s}(\mathbf{x}), \quad (2.13)$$

where the integration is over the entire volume of the system.[18] Now since $\Delta(\mathbf{x}-\mathbf{q}_i)$ is defined so that it is zero except in a small region, the volume integrals of the derivatives of $\Delta(\mathbf{x}-\mathbf{q}_i)$ are negligible. Consequently, the integration (2.13) yields[19]

$$\mathbf{S}=\frac{1}{2V}\Big\{\sum_i\frac{\mathbf{p}_i}{m_i}\Big(\frac{p_i^2}{2m_i}+V_i\Big)$$
$$+\sum_{ij}(\mathbf{q}_i-\mathbf{q}_j)\frac{1}{i\hbar}\Big[\frac{p_i^2}{2m_i},V_j\Big]\Big\}+\text{H.c.} \quad (2.14)$$

Although the interest here is in solids, the above formulas for $\mathbf{s}(\mathbf{x})$ and $\mathbf{S}$ are also valid for gases and liquids. In particular, the first terms (those containing the product of three momentum operators) give the significant contribution to the flux in a low-density gas.

3. THE HARMONIC ENERGY FLUX

The Hamiltonian will be written as

$$H=H^0+\lambda H', \quad (3.1)$$

where H^0 is the harmonic Hamiltonian for a lattice, $\lambda H'$ describes the effects of imperfections and anharmonic forces, and λ characterizes the strength of this perturbation. With this and an analogous separation of the energy density, the energy-flux operator can be expressed as

$$\mathbf{S}=\mathbf{S}^0+\lambda\mathbf{S}'+\lambda^2\mathbf{S}'', \quad (3.2)$$

where S^0 is independent of the perturbation and where, as is indicated, $\lambda\mathbf{S}'$ and $\lambda^2\mathbf{S}''$ are proportional to λ and λ^2. In this section the harmonic contribution to the average flux $\mathbf{S}^0$ is expressed as a function of the creation and annihilation operators for phonons; the contributions $\lambda\mathbf{S}'$ and $\lambda^2\mathbf{S}''$ are discussed in Sec. 4. For simplicity only a cubic lattice with one atom per unit cell is considered, but this restriction is not fundamental, and the techniques utilized also apply to more complex structures.

Introduction of Phonons

Before proceeding, the notation to be used for the phonon description of lattice dynamics will be introduced.[20]

The momentum and position operators for the ith particle in a lattice will be designated $\mathbf{P}(\mathbf{x}_i)$ and $\mathbf{Q}(\mathbf{x}_i)$, respectively, where $\mathbf{Q}(\mathbf{x}_i)$ measures the displacement of the ith particle from its equilibrium position (or lattice site) $\mathbf{x}_i$. These operators are related to the $\mathbf{p}_i$ and $\mathbf{q}_i$ in the previous section by

$$\mathbf{P}(\mathbf{x}_i)=\mathbf{p}_i \quad \text{and} \quad \mathbf{Q}(\mathbf{x}_i)=\mathbf{q}_i-\mathbf{x}_i, \quad (3.3)$$

since it was implicit that the $\mathbf{q}_i$ were measured from a common origin.

The harmonic part of the Hamiltonian is written as

$$H^0=\frac{1}{2m}\sum_i P(\mathbf{x}_i)^2$$
$$+\tfrac{1}{2}\sum_{ij}\sum_{ab}A^{ab}(\mathbf{x}_i-\mathbf{x}_j)Q^a(\mathbf{x}_i)Q^b(\mathbf{x}_j), \quad (3.4)$$

where m is the mass of the particles, and the coefficients $A^{ab}(\mathbf{x}_i)$ satisfy the relations

$$A^{ba}(-\mathbf{x}_i)=A^{ab}(\mathbf{x}_i)=A^{ba}(\mathbf{x}_i). \quad (3.5)$$

The harmonic Hamiltonian is expressible as a sum of independent harmonic oscillator Hamiltonians by using the transformation

$$\mathbf{P}(\mathbf{x}_i)=N^{-1/2}\sum_{\mathbf{k}s}p_{\mathbf{k}s}\mathbf{e}_{\mathbf{k}s}e^{i\mathbf{k}\cdot\mathbf{x}_i},$$
$$\mathbf{Q}(\mathbf{x}_i)=N^{-1/2}\sum_{\mathbf{k}s}q_{\mathbf{k}s}{}^\dagger\mathbf{e}_{\mathbf{k}s}e^{i\mathbf{k}\cdot\mathbf{x}_i}, \quad (3.6)$$

where N is the total number of particles in the system, $q_{\mathbf{k}s}{}^\dagger$ is the Hermitian conjugate of $q_{\mathbf{k}s}$, and where

$$p_{\mathbf{k}s}=-p_{-\mathbf{k}s}{}^\dagger \quad \text{and} \quad q_{\mathbf{k}s}=-q_{-\mathbf{k}s}{}^\dagger. \quad (3.7)$$

The polarization vectors $\mathbf{e}_{\mathbf{k}s}$ and the frequencies $\omega_{\mathbf{k}s}$ are determined by

$$m\omega_{\mathbf{k}s}{}^2e_{\mathbf{k}s}{}^a=\sum_b\Big(\sum_i A^{ab}(\mathbf{x}_i)e^{i\mathbf{k}\cdot\mathbf{x}_i}\Big)e_{\mathbf{k}s}{}^b, \quad (3.8)$$

or

$$m\omega_{\mathbf{k}s}{}^2\delta_{ss'}=\sum_{ab}e_{\mathbf{k}s}{}^a\Big(\sum_i A^{ab}(\mathbf{x}_i)e^{i\mathbf{k}\cdot\mathbf{x}_i}\Big)e_{\mathbf{k}s'}{}^b, \quad (3.9)$$

[17] By assuming two-body central forces and that the local mean velocity is zero, one can show that the classical analog of (2.12) is equivalent to Irving and Kirkwood's (see Ref. 8) Eqs. (6.20), (6.21), and (6.22).

[18] The integration may be taken over all space as the integrand is zero outside of the system.

[19] By assuming two-body central forces the classical analog of (2.14) becomes equivalent to Eisenschitz's (see Ref. 9) Eq. (1.13).

[20] For general discussions see, e.g., M. Born and K. Huang, *Dynamical Theory of Lattices* (Oxford University Press, London, 1954), or J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1962).

and

$$\mathbf{e}_{\mathbf{k}s}\cdot\mathbf{e}_{\mathbf{k}s'}=\delta_{ss'};\quad \mathbf{e}_{\mathbf{k}s}=-\mathbf{e}_{-\mathbf{k}s};\quad \omega_{\mathbf{k}s}=\omega_{-\mathbf{k}s}. \tag{3.10}$$

The properties (3.5) allow one to replace $e^{i\mathbf{k}\cdot\mathbf{x}_i}$ with $\cos\mathbf{k}\cdot\mathbf{x}_i$ in (3.8) and (3.9). Periodic boundary conditions are imposed to determine the allowed values of $\mathbf{k}$. These values are such that

$$\sum_i e^{i\mathbf{k}\cdot\mathbf{x}_i}=N\Delta_{\mathbf{k}}, \tag{3.11}$$

where $\Delta_{\mathbf{k}}$ equals 1 when $\mathbf{k}=0$, $\mathbf{K}$ (where $\mathbf{K}$ is a member of the reciprocal lattice) and is zero otherwise.

The creation and annihilation operators for phonons, $a_{\mathbf{k}s}^\dagger$ and $a_{\mathbf{k}s}$ respectively, are introduced through the transformation

$$\begin{aligned} p_{\mathbf{k}s}&=-i(\tfrac{1}{2}m\hbar\omega_{\mathbf{k}s})^{1/2}(a_{\mathbf{k}s}+a_{-\mathbf{k}s}^\dagger),\\ q_{\mathbf{k}s}^\dagger&=(\hbar/2m\omega_{\mathbf{k}s})^{1/2}(a_{\mathbf{k}s}-a_{-\mathbf{k}s}^\dagger), \end{aligned} \tag{3.12}$$

where $a_{\mathbf{k}s}^\dagger$ and $a_{\mathbf{k}s}$ satisfy the commutation relations

$$[a_{\mathbf{k}s},a_{\mathbf{k}'s'}^\dagger]=\delta_{\mathbf{k}\mathbf{k}'}\delta_{ss'}. \tag{3.13}$$

The introduction of $a_{\mathbf{k}s}^\dagger$ and $a_{\mathbf{k}s}$ into H^0 yields

$$H^0=\sum_{\mathbf{k}s}(N_{\mathbf{k}s}+\tfrac{1}{2})\hbar\omega_{\mathbf{k}s}, \tag{3.14}$$

where $N_{\mathbf{k}s}=a_{\mathbf{k}s}^\dagger a_{\mathbf{k}s}$ is interpreted as the number of phonons in the $\mathbf{k}s$th normal mode. The matrix representation which diagonalizes the operators $N_{\mathbf{k}s}$ also diagonalizes H^0 and will be referred to as the phonon representation.

The Contribution S^0

The transformation (3.3) implies that

$$\mathbf{q}_i-\mathbf{q}_j=\mathbf{Q}(\mathbf{x}_j)-\mathbf{Q}(\mathbf{x}_j)+\mathbf{x}_i-\mathbf{x}_j. \tag{3.15}$$

Then since the potential energy part of H^0 is a quadratic function of the $\mathbf{Q}(\mathbf{x}_i)$, it follows from (2.14) that

$$\mathbf{S}^0=\mathbf{S}_2{}^0+\mathbf{S}_3{}^0, \tag{3.16}$$

where $\mathbf{S}_2{}^0$ is a quadratic function of the $\mathbf{P}(\mathbf{x}_i)$ and $\mathbf{Q}(\mathbf{x}_i)$ and $\mathbf{S}_3{}^0$ is a cubic function. The term $\mathbf{S}_2{}^0$ is

$$\mathbf{S}_2{}^0=\frac{1}{2mV}\sum_{ij}(\mathbf{x}_i-\mathbf{x}_j)\sum_a\left\{P^a(\mathbf{x}_i)\frac{1}{i\hbar}[P^a(\mathbf{x}_i),V(\mathbf{x}_j)]+\frac{1}{i\hbar}[P^a(\mathbf{x}_i),V(\mathbf{x}_j)]P^a(\mathbf{x}_i)\right\}, \tag{3.17}$$

where $V(\mathbf{x}_j)$, corresponding to the term V_j in (2.14), is

$$V(\mathbf{x}_j)=\tfrac{1}{2}\sum_m\sum_{bc}A^{bc}(\mathbf{x}_j-\mathbf{x}_m)Q^b(\mathbf{x}_j)Q^c(\mathbf{x}_m). \tag{3.18}$$

This choice for $V(\mathbf{x}_i)$ satisfies the requirement that $\sum_i V(\mathbf{x}_i)$ be equal to the potential part of the harmonic Hamiltonian.

The quantity $\mathbf{S}_3{}^0$ is

$$\begin{aligned}\mathbf{S}_3{}^0=&\frac{1}{2V}\left\{\sum_i\frac{\mathbf{P}(\mathbf{x}_i)}{m}\left[\frac{P(\mathbf{x}_i)^2}{2m}+V(\mathbf{x}_i)\right]\right.\\&+\frac{1}{2m}\sum_{ij}[\mathbf{Q}(\mathbf{x}_i)-\mathbf{Q}(\mathbf{x}_j)]\sum_a\left(P^a(\mathbf{x}_i)\frac{1}{i\hbar}[P^a(\mathbf{x}_i),V(\mathbf{x}_j)]\right.\\&\left.\left.+\frac{1}{i\hbar}[P^a(\mathbf{x}_i),V(\mathbf{x}_j)]P^a(\mathbf{x}_i)\right)\right\}+\text{H.c.}\end{aligned} \tag{3.19}$$

The Quadratic Part $S_2{}^0$

Now consider the term $\mathbf{S}_2{}^0$. Using the commutation relations for the $\mathbf{P}(\mathbf{x}_i)$ and $\mathbf{Q}(\mathbf{x}_i)$ one obtains for $\mathbf{x}_i\neq\mathbf{x}_j$

$$(i\hbar)^{-1}[P^a(\mathbf{x}_i),V(\mathbf{x}_j)]=-\tfrac{1}{2}\sum_b A^{ab}(\mathbf{x}_i-\mathbf{x}_j)Q^b(\mathbf{x}_j). \tag{3.20}$$

The introduction of this into (3.17) yields

$$\mathbf{S}_2{}^0=\frac{-1}{2mV}\sum_{jm}\sum_{ab}A^{ab}(\mathbf{x}_m)\mathbf{x}_m P^a(\mathbf{x}_m+\mathbf{x}_j)Q^b(\mathbf{x}_j), \tag{3.21}$$

where $\mathbf{x}_m=\mathbf{x}_i-\mathbf{x}_j$. The introduction of the normal coordinates of H^0 gives

$$\mathbf{S}_2{}^0=\frac{1}{2mV}\sum_{\mathbf{k}ss'}p_{\mathbf{k}s}q_{-\mathbf{k}s'}\sum_{ab}e_{\mathbf{k}s}{}^a\times\Big(\sum_m A^{ab}(\mathbf{x}_m)\mathbf{x}_m e^{i\mathbf{k}\cdot\mathbf{x}_m}\Big)e_{\mathbf{k}s'}{}^b. \tag{3.22}$$

At this point it is convenient to introduce a quantity $\mathbf{v}_{\mathbf{k}ss'}$:

$$\mathbf{v}_{\mathbf{k}ss'}=\frac{i}{2m(\omega_{\mathbf{k}s}\omega_{\mathbf{k}s'})^{1/2}}\sum_{ab}e_{\mathbf{k}s}{}^a\times\Big(\sum_m A^{ab}(\mathbf{x}_m)\mathbf{x}_m e^{i\mathbf{k}\cdot\mathbf{x}_m}\Big)e_{\mathbf{k}s'}{}^b, \tag{3.23}$$

which has the units of velocity. From this and (3.3) it follows that $\mathbf{v}_{\mathbf{k}ss'}$ is real and that

$$\mathbf{v}_{\mathbf{k}ss'}=\mathbf{v}_{\mathbf{k}s's}=-\mathbf{v}_{-\mathbf{k}s's}. \tag{3.24}$$

Now it will be shown that $\mathbf{v}_{\mathbf{k}ss}(s=s')$ is equal to the group velocity $\nabla_{\mathbf{k}}\omega_{\mathbf{k}s}$. By considering $\omega_{\mathbf{k}s}$ as defined by (3.9) as a continuous function of the wave vector $\mathbf{k}$ and differentiating with respect to k^l (the lth vector component of $\mathbf{k}$), one obtains

$$\begin{aligned}2m\delta_{ss'}\omega_{\mathbf{k}s}\frac{\partial\omega_{\mathbf{k}s}}{\partial k^l}=&\,i\sum_{ab}e_{\mathbf{k}s}{}^a\Big(\sum_m A^{ab}(\mathbf{x}_m)x_m{}^l e^{i\mathbf{k}\cdot\mathbf{x}_m}\Big)e_{\mathbf{k}s'}{}^b\\&+\sum_a\left(\frac{\partial e_{\mathbf{k}s}{}^a}{\partial k^l}\right)m\omega_{\mathbf{k}s'}{}^2e_{ks'}{}^a+\sum_b m\omega_{\mathbf{k}s}{}^2e_{\mathbf{k}s}{}^b\left(\frac{\partial e_{\mathbf{k}s'}{}^b}{\partial k^l}\right),\end{aligned} \tag{3.25}$$

where (3.8) has been used to simplify the last two terms.

Since the polarization vector $\mathbf{e}_{\mathbf{k}s}$ is of unit length, any infinitesimal change in $\mathbf{e}_{\mathbf{k}s}$ resulting from a change in $\mathbf{k}$ must be perpendicular to it, and thus

$$\sum_a (\partial e_{\mathbf{k}s}{}^a/\partial k^l) e_{\mathbf{k}s}{}^a = 0. \tag{3.26}$$

With this relation it follows from a comparison of (3.23) and (3.25) with $s=s'$ that

$$\partial\omega_{\mathbf{k}s}/\partial k^l = v_{\mathbf{k}ss}{}^l \equiv v_{\mathbf{k}s}{}^l, \tag{3.27}$$

where $v_{\mathbf{k}ss}{}^l$ has been written as $v_{\mathbf{k}s}{}^l$ for brevity. Thus one sees that $\mathbf{v}_{\mathbf{k}s}$ is indeed equal to the group velocity.

Another useful result is obtained from (3.25) for $s\neq s'$ in those cases where the frequencies $\omega_{\mathbf{k}s}$ and $\omega_{\mathbf{k}s'}$ happen to coincide. Rewriting the first term on the right of (3.25) with the aid of (3.23) and taking $\omega_{\mathbf{k}s}=\omega_{\mathbf{k}s'}$, one obtains

$$-v_{\mathbf{k}ss'}{}^l = \tfrac{1}{2}\omega_{\mathbf{k}s}[\partial(\textstyle\sum_a e_{\mathbf{k}s}{}^a e_{\mathbf{k}s'}{}^a)/\partial k^l]. \tag{3.28}$$

Since $\mathbf{e}_{\mathbf{k}s}\cdot\mathbf{e}_{\mathbf{k}s'}=0$ when $s\neq s'$, it follows that $\mathbf{v}_{\mathbf{k}ss'}$ is zero when $\omega_{\mathbf{k}s}=\omega_{\mathbf{k}s'}$.

The final expression for $\mathbf{S}_2{}^0$ is obtained by introducing $\mathbf{v}_{\mathbf{k}ss'}$ and the creation and annihilation operators into Eq. (3.22) to obtain

$$\mathbf{S}_2{}^0 = \mathbf{S}_{2,d}{}^0 + \mathbf{S}_{2,nd}{}^0, \tag{3.29}$$

with

$$\mathbf{S}_{2,d}{}^0 = V^{-1}\sum_{\mathbf{k}s} N_{\mathbf{k}s}\hbar\omega_{\mathbf{k}s}\mathbf{v}_{\mathbf{k}s}, \tag{3.30}$$

$$\mathbf{S}_{2,nd}{}^0 = -\frac{1}{2V}\sum_{\mathbf{k}ss',s\neq s'}(a_{\mathbf{k}s}+a_{-\mathbf{k}s}{}^\dagger) \times(a_{-\mathbf{k}s'}-a_{-\mathbf{k}s'}{}^\dagger)\hbar\omega_{\mathbf{k}s}\mathbf{v}_{\mathbf{k}ss'}, \tag{3.31}$$

and $N_{\mathbf{k}s}=a_{\mathbf{k}s}{}^\dagger a_{\mathbf{k}s}$. The subscripts d and nd indicate that $\mathbf{S}_{2,nd}{}^0$ and $\mathbf{S}_{2,nd}{}^0$ are respectively, diagonal and nondiagonal matrices in the phonon representation. (Since $\mathbf{S}_3{}^0$ is a cubic function of the $a_{\mathbf{k}s}{}^\dagger$ and $a_{\mathbf{k}s}$, it is necessarily nondiagonal.) One now has the important result that the usual expression for the energy-flux operator in a lattice, that is, Eq. (3.30) or (1.1) is just the diagonal part of the harmonic contribution.

The significance of the term $\mathbf{S}_{2,nd}{}^0$ is most easily understood in the classical limit. Expressing (3.31) in terms of the normal mode variables $p_{\mathbf{k}s}$ and $q_{\mathbf{k}s}{}^\dagger$, one gets

$$\mathbf{S}_{2,nd}{}^0 = i\sum_{\mathbf{k}ss',s\neq s'} p_{\mathbf{k}s}q_{-\mathbf{k}s'}{}^\dagger(\omega_{\mathbf{k}s}\omega_{\mathbf{k}s'})^{1/2}\mathbf{v}_{\mathbf{k}ss'}, \tag{3.32}$$

and the classical limit is obtained by simply treating $p_{\mathbf{k}s}$ and $q_{-\mathbf{k}s'}{}^\dagger$ as classical variables (with the Hermitian conjugate becoming a complex conjugate). The variables $p_{\mathbf{k}s}$ and $q_{-\mathbf{k}s'}{}^\dagger$ are then rapidly oscillating functions of time with frequencies $\omega_{\mathbf{k}s}$ and $\omega_{\mathbf{k}s'}$. As $\omega_{\mathbf{k}s}$ is unequal to $\omega_{\mathbf{k}s'}$ for those terms with $s\neq s'$ and $\mathbf{v}_{\mathbf{k}ss'}\neq 0$ [see (3.28)], it follows that (3.32) is made up of oscillating terms with frequencies which are the sums and differences of $\omega_{\mathbf{k}s}$ and $\omega_{\mathbf{k}s'}$. As a result, when the flux is averaged over long periods of time (i.e., over many periods of oscillation), the contribution of $\mathbf{S}_{2,nd}{}^0$ to the transport of energy is negligible compared to that of the (classically time-independent) contribution $\mathbf{S}_{2,d}{}^0$. (It is interesting to note that terms analogous to $\mathbf{S}_{2,nd}{}^0$ also exist in the expression for the flux for an isotropic elastic medium.[21])

The Cubic Part $\mathbf{S}_3{}^0$

The term $\mathbf{S}_3{}^0$ is easily expressed as a function of the $p_{\mathbf{k}s}$ and $q_{\mathbf{k}s}$ by applying the transformation (3.6) to Eq. (3.19) for $\mathbf{S}_3{}^0$. The result is

$$\mathbf{S}_3{}^0 = \frac{1}{4VN^{1/2}}\sum_{\mathbf{k}\mathbf{k}'\mathbf{k}'',ss's''}\mathbf{e}_{\mathbf{k}s}(\mathbf{e}_{\mathbf{k}'s'}\ \mathbf{e}_{\mathbf{k}''s''})\Delta_{\mathbf{k}+\mathbf{k}'+\mathbf{k}''} \times\left\{\frac{p_{\mathbf{k}s}p_{\mathbf{k}'s'}p_{\mathbf{k}''s''}}{m^2} + p_{\mathbf{k}s}q_{\mathbf{k}'s'}{}^\dagger q_{\mathbf{k}''s''}{}^\dagger\omega_{\mathbf{k}''s''}{}^2 + q_{\mathbf{k}s}{}^\dagger q_{\mathbf{k}'s'}{}^\dagger p_{\mathbf{k}''s''}(\omega_{\mathbf{k}''s''}{}^2-\omega_{\mathbf{k}'s'}{}^2)\right\} + \text{H.c.}, \tag{3.33}$$

where (3.8) has been used to introduce $\omega_{\mathbf{k}s}{}^2$. This is easily written as a function of $a_{\mathbf{k}s}{}^\dagger$ and $a_{\mathbf{k}s}$ by using transformation (3.12).

The significance of $\mathbf{S}_3{}^0$ is most readily seen by inspecting (3.19). The terms in (3.19) containing products of three $\mathbf{P}(\mathbf{x}_i)$'s correspond to Irving and Kirkwood's "kinetic energy" contribution to the flux.[8] The terms $\mathbf{P}(\mathbf{x}_i)V(\mathbf{x}_i)/m$ describe the transport at the velocity $\mathbf{P}(\mathbf{x}_i)/m$ of the potential energy $V(\mathbf{x}_i)$. The terms containing the difference $\mathbf{Q}(\mathbf{x}_i)-\mathbf{Q}(\mathbf{x}_j)$ are corrections to $\mathbf{S}_2{}^0$ arising from the fact that the interparticle forces do not transmit energy between the lattice sites $\mathbf{x}_i$ and $\mathbf{x}_j$, but between the actual positions of the particles which are displaced from $\mathbf{x}_i$ and $\mathbf{x}_j$ by $\mathbf{Q}(\mathbf{x}_i)$ and $\mathbf{Q}(\mathbf{x}_j)$.

If the energy $(p_i{}^2/2m)+V_i$ were associated with the lattice site $\mathbf{x}_i$ instead of with the actual position of the particle $\mathbf{q}_i=\mathbf{Q}(\mathbf{x}_i)+\mathbf{x}_i$, the contribution $\mathbf{S}_2{}^0$ would be obtained, but not $\mathbf{S}_3{}^0$. This is easily seen by retracing the calculations of Sec. 2 with $\Delta(\mathbf{x}-\mathbf{q}_i)$ replaced by $\Delta(\mathbf{x}-\mathbf{x}_i)$. (Note that since $\mathbf{x}_i$ is a number it commutes with the operator $\mathbf{p}_i$.) Thus, if the particle displacements are small compared to the lattice spacing, the contribution of $\mathbf{S}_3{}^0$ to the flux will be small compared to that of $\mathbf{S}_2{}^0$. This will actually be the case except at elevated temperatures.

4. PERTURBATION CONTRIBUTION TO THE ENERGY FLUX

The contribution to the average energy flux from the anharmonic forces and lattice imperfections will now be treated. The perturbation due to the anharmonic forces

[21] R. J. Hardy, Ph.D. thesis, Lehigh University (University Microfilms, 1962), p. 96.

that is considered is

$$\lambda V_3=\frac{1}{3!}\sum_{ijm}\sum_{abc}B^{abc}(\mathbf{x}_i,\mathbf{x}_j,\mathbf{x}_m)Q^a(\mathbf{x}_i)Q^b(\mathbf{x}_j)Q^c(\mathbf{x}_m), \quad (4.1)$$

which is the cubic term in the potential energy expansion. The effects of imperfections are not included in λV_3, so that one has

$$B^{abc}(\mathbf{x}_i,\mathbf{x}_j,\mathbf{x}_m)=B^{abc}(0,\ \mathbf{x}_j-\mathbf{x}_i,\ \mathbf{x}_m-\mathbf{x}_i). \quad (4.2)$$

The correction to the kinetic energy arising from the presence of impurities, isotopes, etc., is

$$\lambda T'=-\frac{1}{2m}\sum_i\frac{\delta m_i}{m+\delta m_i}P(\mathbf{x}_i)^2, \quad (4.3)$$

where

$$\delta m_i=m_i-m, \quad (4.4)$$

where m_i is the actual mass of particle i [see (2.4)] and m is the mass used in H^0 [see (3.4)]. Lattice imperfections also give rise to a perturbation[22]

$$\lambda V_2=\tfrac{1}{2}\sum_{ij}\sum_{mn}C^{ab}(\mathbf{x}_i,\mathbf{x}_j)Q^a(\mathbf{x}_i)Q^b(\mathbf{x}_j), \quad (4.5)$$

where the coefficient $C^{ab}(\mathbf{x}_i,\mathbf{x}_j)$ are the corrections to the quadratic term in the potential energy expansion, the complete coefficients being $A^{ab}(\mathbf{x}_i-\mathbf{x}_j)+C^{ab}(\mathbf{x}_i,\mathbf{x}_j)$. In general, $C^{ab}(\mathbf{x}_i,\mathbf{x}_j)$ depends on the specific positions in the lattice of both the particles i and j, while $A^{ab}(\mathbf{x}_i-\mathbf{x}_j)$, which is included in H^0, depends on their relative displacement only.

The Contribution from λV_3

From (2.14) it follows that the contribution of λV_3 to the average energy flux $\lambda\mathbf{S}_V'$ is

$$\lambda\mathbf{S}'_V=(2V)^{-1}\{m^{-1}\sum_i\mathbf{P}(\mathbf{x}_i)\lambda V_3(\mathbf{x}_i)+(2m)^{-1}\sum_{ij}[\mathbf{Q}(\mathbf{x}_i)-\mathbf{Q}(\mathbf{x}_j)+\mathbf{x}_i-\mathbf{x}_j]\times(i\hbar)^{-1}[P(\mathbf{x}_i)^2,\lambda V_3(\mathbf{x}_j)]\}+\text{H.c.} \quad (4.6)$$

The form of λV_3 suggests that one take

$$\lambda V_3(\mathbf{x}_i)=\frac{1}{3!}\sum_{jm}\sum_{abc}B^{abc}(\mathbf{x}_i,\mathbf{x}_j,\mathbf{x}_m)\times Q^a(\mathbf{x}_i)Q^b(\mathbf{x}_j)Q^c(\mathbf{x}_m). \quad (4.7)$$

Just as H^0, a quadratic function of the $\mathbf{P}(\mathbf{x}_i)$ and $\mathbf{Q}(\mathbf{x}_i)$, led to $\mathbf{S}^0=\mathbf{S}_2{}^0+\mathbf{S}_3{}^0$, the contribution of λV_3 to the flux can be written as

$$\lambda\mathbf{S}_V'=\lambda\mathbf{S}_3'+\lambda\mathbf{S}_4', \quad (4.8)$$

where $\mathbf{S}_3'$ and $\mathbf{S}_4'$ are, respectively, cubic and quartic functions of the $\mathbf{P}(\mathbf{x}_i)$ and $\mathbf{Q}(\mathbf{x}_i)$.

The quantity $\lambda\mathbf{S}_3'$ will be treated first. By using (4.7) and the commutation relations it can be shown for $\mathbf{x}_i\neq\mathbf{x}_j$ that

$$(i\hbar)^{-1}[P(\mathbf{x}_i)^2,\lambda V_3(\mathbf{x}_j)]=-\tfrac{1}{3}\sum_m\sum_{abc}B^{abc}(\mathbf{x}_i,\mathbf{x}_j,\mathbf{x}_m)\times(P^a(\mathbf{x}_i)Q^b(\mathbf{x}_j)Q^c(\mathbf{x}_m)+Q^b(\mathbf{x}_j)Q^c(\mathbf{x}_m)P^a(\mathbf{x}_i)). \quad (4.9)$$

Multiplying this result by $(2m)^{-1}(\mathbf{x}_i-\mathbf{x}_j)$, summing over i and j, and introducing the creation and annihilation operators, one obtains

$$\lambda\mathbf{S}_3'=\frac{1}{2V}\sum_{\mathbf{k}\mathbf{k}'\mathbf{k}'',ss's''}\mathbf{B}_{\mathbf{k}s,\mathbf{k}'s',\mathbf{k}''s''}\left\{-i\left(\frac{\hbar^3\omega_{\mathbf{k}s}}{8m\omega_{\mathbf{k}'s'}\omega_{\mathbf{k}''s''}}\right)^{1/2}\times(a_{\mathbf{k}s}+a_{-\mathbf{k}s}{}^\dagger)(a_{\mathbf{k}'s'}-a_{-\mathbf{k}'s'}{}^\dagger)\times(a_{\mathbf{k}''s''}-a_{-\mathbf{k}''s''}{}^\dagger)\right\}+\text{H.c.}, \quad (4.10)$$

where

$$\mathbf{B}_{\mathbf{k}s,\mathbf{k}'s',\mathbf{k}''s''}=\frac{1}{3mN^{1/2}}\Delta_{\mathbf{k}+\mathbf{k}'+\mathbf{k}''}\sum_{abc}e_{\mathbf{k}s}{}^a e_{\mathbf{k}'s'}{}^b e_{\mathbf{k}''s''}{}^c\times\sum_{mn}B^{abc}(0,\mathbf{x}_m,\mathbf{x}_n)\mathbf{x}_m e^{i(\mathbf{k}'\cdot\mathbf{x}_m+\mathbf{k}''\cdot\mathbf{x}_n)}. \quad (4.11)$$

The quantity inside the curly brackets in (4.10) is just $p_{\mathbf{k}s}q_{\mathbf{k}'s'}{}^\dagger q_{\mathbf{k}''s''}{}^\dagger$. Notice that

$$\mathbf{B}_{\mathbf{k}s,\mathbf{k}'s',\mathbf{k}''s''}=-\mathbf{B}^*{}_{-\mathbf{k}s,-\mathbf{k}'s',-\mathbf{k}''s''}, \quad (4.12)$$

where the asterisk indicates complex conjugation.

The quartic term $\lambda\mathbf{S}_4'$ can be written with the aid of (4.7) and (4.6) [in (4.6) replace $\mathbf{Q}(\mathbf{x}_i)-\mathbf{Q}(\mathbf{x}_j)+\mathbf{x}_i-\mathbf{x}_j$ by $\mathbf{Q}(\mathbf{x}_i)-\mathbf{Q}(\mathbf{x}_j)$] as

$$\lambda S_4'{}^l=\frac{1}{2V3!m}\sum_{ijm}\sum_{abc}B^{abc}(\mathbf{x}_i,\mathbf{x}_j,\mathbf{x}_m)\times\{Q^a(\mathbf{x}_i)Q^b(\mathbf{x}_j)Q^c(\mathbf{x}_m)P^l(\mathbf{x}_i)-2Q^l(\mathbf{x}_i)Q^b(\mathbf{x}_j)Q^c(\mathbf{x}_m)P^a(\mathbf{x}_i)+2Q^l(\mathbf{x}_j)Q^b(\mathbf{x}_j)Q^c(\mathbf{x}_m)P^a(\mathbf{x}_i)\}+\text{H.c.} \quad (4.13)$$

The introduction of $a_{\mathbf{k}s}{}^\dagger$ and $a_{\mathbf{k}s}$ yields

$$\lambda\mathbf{S}_4'=\frac{1}{2V}\sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}''',ss's''s'''}\mathbf{B}_{\mathbf{k}s,\mathbf{k}'s',\mathbf{k}''s'',\mathbf{k}'''s'''}\times\left\{\frac{-i\hbar^2}{4m}\left(\frac{\omega_{\mathbf{k}'''s'''}}{\omega_{\mathbf{k}s}\omega_{\mathbf{k}'s'}\omega_{\mathbf{k}''s''}}\right)^{1/2}\times(a_{\mathbf{k}s}-a_{-\mathbf{k}s}{}^\dagger)(a_{\mathbf{k}'s'}-a_{-\mathbf{k}'s'}{}^\dagger)(a_{\mathbf{k}''s''}-a_{-\mathbf{k}''s''}{}^\dagger)\times(a_{\mathbf{k}'''s'''}+a_{-\mathbf{k}'''s'''}{}^\dagger)\right\}+\text{H.c.}, \quad (4.14)$$

[22] For convenience, the same parameter λ is used to characterize the strength of the different perturbations λV_3, $\lambda T'$, and λV_2 even though they are in reality all independent.

where

$$\mathbf{B}_{\mathbf{k}s,\mathbf{k}'s',\mathbf{k}''s'',\mathbf{k}'''s'''}$$
$$=\frac{1}{3!mN}\Delta_{\mathbf{k}+\mathbf{k}'+\mathbf{k}''+\mathbf{k}'''}\sum_{abc}e_{\mathbf{k}'s'}{}^{b}e_{\mathbf{k}''s''}{}^{c}$$
$$\times\sum_{mn}B^{abc}(0,\mathbf{x}_m,\mathbf{x}_n)e^{i(\mathbf{k}'\cdot\mathbf{x}_m+\mathbf{k}''\cdot\mathbf{x}_n)}$$
$$\times[e_{\mathbf{k}s}{}^{a}\mathbf{e}_{\mathbf{k}'''s'''}+2\mathbf{e}_{\mathbf{k}s}e_{\mathbf{k}'''s'''}{}^{a}(e^{i\mathbf{k}\cdot\mathbf{x}_m}-1)]. \quad (4.15)$$

The quantity inside the curly brackets in (4.14) is $q_{\mathbf{k}s}{}^{\dagger}q_{\mathbf{k}'s'}{}^{\dagger}q_{\mathbf{k}''s''}{}^{\dagger}p_{\mathbf{k}'''s'''}$. Notice that

$$\mathbf{B}_{\mathbf{k}s,\mathbf{k}'s',\mathbf{k}''s'',\mathbf{k}'''s'''}=\mathbf{B}_{-\mathbf{k}s,-\mathbf{k}'s',-\mathbf{k}''s'',-\mathbf{k}'''s'''}{}^{*}. \quad (4.16)$$

The complete expression for the contribution of λV_3 to the flux is obtained by combining (4.8), (4.10), and (4.14).

The Contributions from $\lambda T'$ and λV_2

The effect of lattice imperfections on the part of the energy flux proportional to λ will now be treated.[22] It can be deduced from (2.14) that the kinetic-energy perturbation $\lambda T'$ gives a contribution $\lambda\mathbf{S}_{T'}$ to the average flux of the form

$$\lambda\mathbf{S}_{T'}=\left(\frac{-1}{2V}\right)\Big\{\sum_i\frac{\delta m_i}{m^2}\frac{m+\frac{1}{2}\delta m_i}{(m+\delta m_i)^2}\mathbf{P}(\mathbf{x}_i)P(\mathbf{x}_i)^2$$
$$+\frac{1}{m}\sum_i\frac{\delta m_i}{m+\delta m_i}\mathbf{P}(\mathbf{x}_i)V(\mathbf{x}_i)$$
$$+\frac{1}{2m}\sum_{ij}(\mathbf{Q}(\mathbf{x}_i)-\mathbf{Q}(\mathbf{x}_j)+\mathbf{x}_i-\mathbf{x}_j)$$
$$\times\frac{\delta m_i}{m+\delta m_i}\frac{1}{i\hbar}[P(\mathbf{x}_i)^2,V(\mathbf{x}_j)]\Big\}+\text{H.c.}, \quad (4.17)$$

where $V(\mathbf{x}_i)$ is the potential energy part of the harmonic Hamiltonian given in (3.18). The contribution of λV_2 to the flux is given by an equation of the form of (4.6) with $\lambda V_3(\mathbf{x}_i)$ replaced by

$$\lambda V_2(\mathbf{x}_i)=\tfrac{1}{2}\sum_j\sum_{ab}C^{ab}(\mathbf{x}_i,\mathbf{x}_j)Q^a(\mathbf{x}_i)Q^b(\mathbf{x}_j). \quad (4.18)$$

These contributions to the flux are readily expressed as functions of the creation and annihilation operators, but the complete calculation will not be given here. However, it will be shown that if the Hamiltonian is separated into parts $H=H^0+\lambda H'$ in such a way that the perturbations $\lambda T'$ and λV_2 are nondiagonal in the phonon representation, then the contributions of these perturbations to the flux are also nondiagonal.

The conditions under which $\lambda T'$ and λV_2 are nondiagonal can be seen by transforming (4.3) and (4.5) to phonon variables, which gives

$$\lambda T'=\tfrac{1}{4}\hbar\sum_{\mathbf{k}\mathbf{k}',ss'}(a_{\mathbf{k}s}+a_{-\mathbf{k}s}{}^{\dagger})(a_{\mathbf{k}'s'}+a_{-\mathbf{k}'s'}{}^{\dagger})(\omega_{\mathbf{k}s}\omega_{\mathbf{k}'s'})^{1/2}$$
$$\times(\mathbf{e}_{\mathbf{k}s}\cdot\mathbf{e}_{\mathbf{k}'s'})\Big\{N^{-1}\sum_i\frac{\delta m_i}{m+\delta m_i}e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{x}_i}\Big\} \quad (4.19)$$

and

$$\lambda V_2=\frac{\hbar}{4m}\sum_{\mathbf{k}\mathbf{k}',ss'}(a_{\mathbf{k}s}-a_{-\mathbf{k}s}{}^{\dagger})(a_{\mathbf{k}'s'}-a_{-\mathbf{k}'s'}{}^{\dagger})$$
$$\times(\omega_{\mathbf{k}s}\omega_{\mathbf{k}'s'})^{-1/2}\sum_{ab}e_{\mathbf{k}s}{}^{a}e_{\mathbf{k}'s'}{}^{b}$$
$$\times\sum_m\{N^{-1}\sum_i C^{ab}(\mathbf{x}_i,\mathbf{x}_i-\mathbf{x}_m)e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{x}_i}\}e^{-i\mathbf{k}'\cdot\mathbf{x}_m}. \quad (4.20)$$

Diagonal terms in the phonon representation can occur only when $\mathbf{k}=-\mathbf{k}'$ (and $s=s'$). The factors in curly brackets in (4.19) and (4.20) are zero for $\mathbf{k}=-\mathbf{k}'$ when the δm_i and $C^{ab}(\mathbf{x}_i,\mathbf{x}_j)$ are chosen so that

$$N^{-1}\sum_i\frac{\delta m_i}{m+\delta m_i}=0, \quad (4.21)$$

and

$$N^{-1}\sum_i C^{ab}(\mathbf{x}_i,\mathbf{x}_i-\mathbf{x}_m)=0. \quad (4.22)$$

A comparison of (4.21) with (4.4) indicates that condition (4.21) can be satisfied by defining m as

$$\frac{1}{m}=N^{-1}\sum_i\frac{1}{m+\delta m_i}=N^{-1}\sum_i\frac{1}{m_i}. \quad (4.23)$$

Also, it is always possible to choose the $A^{ab}(\mathbf{x}_i-\mathbf{x}_j)$ and $C^{ab}(\mathbf{x}_i,\mathbf{x}_j)$ so that condition (4.22) is fulfilled [see discussion following (4.5)]. If these conditions are not initially satisfied, they can be obtained by redefining m and the $C^{ab}(\mathbf{x}_i,\mathbf{x}_j)$, and correcting the frequencies and polarization vectors determined by (3.8). Thus, it is always possible to separate the Hamiltonian into parts so that $\lambda T'$ and λV_2 are nondiagonal in the representation diagonalizing H^0.

The conditions (4.21) and (4.22) also cause the contributions of $\lambda T'$ and λV_2 to the energy flux to be nondiagonal. To show this, write out those parts of these contributions which are quadratic in the $\mathbf{P}(\mathbf{x}_i)$ and $\mathbf{Q}(\mathbf{x}_i)$, these being the only parts which could give diagonal matrix elements. One obtains

$$\lambda\mathbf{S}_2'=\left(\frac{-i\hbar}{8mV}\right)\sum_{\mathbf{k}\mathbf{k}',ss'}(a_{\mathbf{k}s}+a_{-\mathbf{k}s}{}^{\dagger})(a_{\mathbf{k}'s'}-a_{-\mathbf{k}'s'}{}^{\dagger})$$
$$\times\left(\frac{\omega_{\mathbf{k}s}}{\omega_{\mathbf{k}'s'}}\right)^{1/2}\sum_{ab}e_{\mathbf{k}s}{}^{a}e_{\mathbf{k}'s'}{}^{b}$$
$$\times\sum_m\Big[\Big\{N^{-1}\sum_i\frac{\delta m_i}{m+\delta m_i}e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{x}_i}\Big\}A^{ab}(\mathbf{x}_m)$$
$$-\{N^{-1}\sum_i C^{ab}(\mathbf{x}_i,\mathbf{x}_i-\mathbf{x}_m)e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{x}_i}\}\Big]$$
$$\times\mathbf{x}_m e^{-i\mathbf{k}'\cdot\mathbf{x}_m}+\text{H.c.} \quad (4.24)$$

Again, diagonal elements can occur only in terms with $\mathbf{k}=-\mathbf{k}'$, but the coefficients of such terms are zero when conditions (4.21) and (4.22) are satisfied. Thus, it is seen that the separation of the Hamiltonian which makes $\lambda T'$ and λV_2 nondiagonal also makes their contributions to the flux nondiagonal. The significance of this is that nondiagonal terms correspond (classically) to oscillatory functions whose contributions to the transport of energy are of a smaller order than those of the (time-independent) diagonal terms.

Other Contributions to the Flux

An inspection of the general expression (2.14) for the energy flux shows that contributions proportional to λ^2 will result from a combination of a kinetic energy and a potential energy perturbation. There are also contributions to the flux from higher powers in the potential energy expansion, which can be treated along essentially the same lines as the contribution from λV_3. In particular, a perturbation which is of nth power in the $\mathbf{Q}(\mathbf{x}_i)$'s gives rise to nth and $(n+1)$st power contributions to the energy flux, just as the cubic perturbation gave cubic and quartic contributions. The calculation of these higher order contributions is straightforward. However, they will not be considered further here.

5. THE LOCAL ENERGY FLUX

In the usual discussion of lattice thermal conductivity, based on the Boltzmann equation, it is necessary to introduce a number operator $N_{\mathbf{k}s}(\mathbf{x})$ which is a function of position. Associated with this is an expression for the local energy flux of the form

$$\mathbf{s}(\mathbf{x})=\sum_{\mathbf{k}s} N_{\mathbf{k}s}(\mathbf{x})\hbar\omega_{\mathbf{k}s}\mathbf{v}_{\mathbf{k}s}. \tag{5.1}$$

One method[2] of justifying this point of view is to divide the lattice into small regions and identify $\mathbf{s}(\mathbf{x})$, for example, with the average energy flux (1.1) of the region containing $\mathbf{x}$. This procedure, however, requires heuristic arguments whose rigorous justification is not readily seen. Another approach is to form wave packets of the plane-wave normal modes,[3] but is is not clear exactly how these packets are to be formed. In this section the rigorous expression (2.12) for the local energy flux operator will be used to determine just what approximations are necessary to obtain an expression of the form (5.1) and to give a more precise meaning to the quantity $N_{\mathbf{k}s}(\mathbf{x})$.

First, those terms in the exact expression for the local flux analogous to $\lambda\mathbf{S}'$ (the perturbation contribution to the flux) and $\mathbf{S}_3{}^0$ (which does not exist when the energy of the particles is identified with the lattice sites) will be neglected. One expects their contributions to be small for the reasons discussed in Secs. 3 and 4. Next, it will be assumed that

$$l_F\ll l, \tag{5.2}$$

where l_F characterizes the interparticle force range, and l is descriptive of the localization of the operators $H(\mathbf{x})$ and $s(\mathbf{x})$ [see the discussion of (2.5)]. The interparticle force range comes into expression (2.12) for $\mathbf{s}(\mathbf{x})$ through $[p_i{}^2,V_j]$ which is zero for $|\mathbf{q}_i-\mathbf{q}_j|>l_F$. The quantity $\Delta(\mathbf{x}-\mathbf{q}_i)/l^n$ gives the order of the nth derivative of $\Delta(\mathbf{x}-\mathbf{q}_i)$ with respect to $\mathbf{x}$ [this can be seen by differentiating (2.7)]. From this it follows that the expansion in (2.12) is an expansion in powers of l_F/l, so that with $l_F\ll l$ the first term in the series is a good approximation to the complete expansion. Thus, using the above approximations and introducing the $\mathbf{P}(\mathbf{x}_i)$ and $\mathbf{Q}(\mathbf{x}_i)$ into (2.12), one obtains

$$\mathbf{s}_2{}^0(\mathbf{x})=\frac{1}{2m}\sum_{ij}\Delta(\mathbf{x}-\mathbf{x}_i)(\mathbf{x}_i-\mathbf{x}_j)\frac{1}{i\hbar}[P(\mathbf{x}_i)^2,V(\mathbf{x}_j)]. \tag{5.3}$$

The introduction of the creation and annihilation operators gives

$$\begin{aligned}\mathbf{s}_2{}^0(\mathbf{x})=\frac{i\hbar}{4m}\sum_{\mathbf{k}\mathbf{k}',ss'}&(a_{-\mathbf{k}'s'}+a_{k's'}{}^\dagger)(a_{\mathbf{k}s}-a_{-\mathbf{k}s}{}^\dagger)\left(\frac{\omega_{\mathbf{k}'s'}}{\omega_{\mathbf{k}s}}\right)^{1/2}\\ &\times\sum_{ab}e_{-\mathbf{k}'s'}{}^a e_{\mathbf{k}s}{}^b\sum_m A^{ab}(\mathbf{x}_m)\mathbf{x}_m e^{-i\mathbf{k}\cdot\mathbf{x}_m}\\ &\times\{N^{-1}\sum_i\Delta(\mathbf{x}-\mathbf{x}_i)e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}_i}\}.\end{aligned} \tag{5.4}$$

As suggested by (2.7), the function $\Delta(\mathbf{x}-\mathbf{x}_i)$ will be taken to be

$$\Delta(\mathbf{x}-\mathbf{x}_i)=\pi^{-3/2}l^{-3}\exp(-|\mathbf{x}-\mathbf{x}_i|^2/l^2). \tag{5.5}$$

With this the term in curly brackets in (5.4) can be written as

$$\frac{1}{N\pi^{3/2}l^3}\sum_i\exp\left(-\frac{|\mathbf{x}_i-\mathbf{b}|^2}{l^2}-\tfrac{1}{4}|\mathbf{k}-\mathbf{k}'|^2l^2+i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}\right), \tag{5.6}$$

where $\mathbf{b}=\mathbf{x}+\frac{1}{2}il^2(\mathbf{k}-\mathbf{k}')$. It will now be assumed that

$$a\ll l\ll L, \tag{5.7}$$

where the lattice constant a gives the value of $|\mathbf{x}_i-\mathbf{x}_j|$ when i and j are adjacent particles, and L characterizes the dimensions of the system being considered. With $l\gg a$ the sum over i in expression (5.6) can be replaced by an integration over $\mathbf{x}_i$, and with $l\ll L$ the limits of integration can be taken to infinity. Carrying out the resulting integral one finds

$$\begin{aligned}&N^{-1}\textstyle\sum_i\Delta(\mathbf{x}-\mathbf{x}_i)\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}_i]\\ &\quad=V^{-1}\exp(-\tfrac{1}{4}|\mathbf{k}-\mathbf{k}'|^2l^2)\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}].\end{aligned} \tag{5.8}$$

The main contribution to (5.4) comes from those values of $\mathbf{k}$ and $\mathbf{k}'$ for which the function $\exp(-\frac{1}{4}|\mathbf{k}-\mathbf{k}'|^2l^2)$ is peaked, i.e., for values which satisfy $|\mathbf{k}-\mathbf{k}'|<2/l$. For such values and with $a\ll l$ it follows from (3.8) and (3.23) that $\mathbf{e}_{-\mathbf{k}'s'}\simeq-\mathbf{e}_{\mathbf{k}s'}$ and $\mathbf{v}_{\mathbf{k}'s's}\simeq\mathbf{v}_{\mathbf{k}s's}$, respectively.

Using these approximations in (5.4), one obtains

$$\mathbf{s}_2^0(\mathbf{x})=\sum_{\mathbf{k}\mathbf{k}',ss'}\frac{1}{2V}(a_{-\mathbf{k}'s'}+a_{\mathbf{k}'s'}^\dagger)(a_{\mathbf{k}s}-a_{-\mathbf{k}s}^\dagger)\times\exp(-\tfrac{1}{4}|\mathbf{k}-\mathbf{k}'|^2l^2)\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}]\times\hbar(\omega_{\mathbf{k}s'}\omega_{\mathbf{k}'s'})^{1/2}\tfrac{1}{2}(\mathbf{v}_{\mathbf{k}s's}+\mathbf{v}_{\mathbf{k}'s's}). \quad (5.9)$$

The terms in (5.9) with $s\neq s'$, which are analogous to $\mathbf{S}_{2,nd}^0$ discussed in Sec. 3, contain contributions from modes with different frequencies, and, thus, are rapidly oscillating functions whose time average is negligible. For this reason they will be neglected. [Of course, the terms being kept with $s=s'$ but $\mathbf{k}\neq\mathbf{k}'$ also possess contributions from modes with different frequencies; however, since the values of $\mathbf{k}$ and $\mathbf{k}'$ can be arbitrarily close (for large systems), the frequency difference $\omega_{\mathbf{k}s}-\omega_{\mathbf{k}'s}$ can be so small that the oscillations are no longer rapid. Although it is also possible for the difference $\omega_{\mathbf{k}s}-\omega_{\mathbf{k}s'}$ with $s\neq s'$ to be very small, the associated terms in $\mathbf{s}_2^0(\mathbf{x})$ still do not contribute because then $\mathbf{v}_{\mathbf{k}ss'}$ is vanishingly small; see (3.28).] Neglecting terms with $s\neq s'$ and using $(\omega_{\mathbf{k}s}\omega_{\mathbf{k}'s})^{1/2}\simeq\omega_{\mathbf{k}s}$, one obtains

$$\mathbf{S}_2^0(\mathbf{x})=\sum_{\mathbf{k}s}N_{\mathbf{k}s}(\mathbf{x})\hbar\omega_{\mathbf{k}s}\mathbf{v}_{\mathbf{k}s}, \quad (5.10)$$

with

$$N_{\mathbf{k}s}(\mathbf{x})=\frac{1}{2V}\sum_{\mathbf{k}'}(a_{\mathbf{k}s}^\dagger a_{\mathbf{k}'s}\exp[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{x}]+\text{H.c.})\times\exp(-\tfrac{1}{4}|\mathbf{k}-\mathbf{k}'|^2l^2). \quad (5.11)$$

Here one has the expression for the local energy flux in the desired form together with an expression for the quantity $N_{\mathbf{k}s}(\mathbf{x})$. The average over the system of (5.10) yields the usual expression (1.1) or (3.30) for the energy flux, since the volume integral of $\exp(i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x})$ equals $V\delta_{\mathbf{k},\mathbf{k}'}$ because of the periodic boundary conditions.

The Conservation of Energy

It will now be shown that $\mathbf{s}_2^0(\mathbf{x})$ as given above satisfies the equation for energy conservation,

$$\dot{H}(\mathbf{x})+\nabla\cdot\mathbf{s}(\mathbf{x})=0, \quad (2.1)$$

in the same approximation that the result (5.10) is valid. To show this the energy density $H(\mathbf{x})$ must first be expressed as a function of the creation and annihilation operators. By approximating the function $\Delta(\mathbf{x}-\mathbf{Q}(\mathbf{x}_i)-\mathbf{x}_i)$ in Eq. (2.5) for $H(\mathbf{x})$ with $\Delta(\mathbf{x}-\mathbf{x}_i)$ and neglecting the perturbations, one obtains

$$H^0(\mathbf{x})=\sum_i\Delta(\mathbf{x}-\mathbf{x}_i)\times\left(\frac{P(\mathbf{x}_i)^2}{2m}+\tfrac{1}{2}\sum_j\sum_{ab}A^{ab}(\mathbf{x}_i-\mathbf{x}_j)Q^a(\mathbf{x}_i)Q^b(\mathbf{x}_j)\right). \quad (5.12)$$

The transformation to the $a_{\mathbf{k}s}^\dagger$ and $a_{\mathbf{k}s}$ with the aid of (5.8) and the approximations $\mathbf{e}_{-\mathbf{k}'s}\cdot\mathbf{e}_{\mathbf{k}s}\simeq-\delta_{ss'}$ and $\omega_{\mathbf{k}s}^2\simeq\omega_{\mathbf{k}'s}\omega_{\mathbf{k}s}\simeq\omega_{\mathbf{k}s}^3/\omega_{\mathbf{k}'s}$ yields

$$H^0(\mathbf{x})=\sum_{\mathbf{k}s}\left(N_{\mathbf{k}s}(\mathbf{x})+\frac{1}{2V}\right)\hbar\omega_{\mathbf{k}s}. \quad (5.13)$$

Notice that the average over the volume of the system of this expression is just H^0/V.

A straightforward calculation making use of the creation and annihilation operators and Eq. (3.14) for H^0 leads to

$$\dot{N}_{\mathbf{k}s}(\mathbf{x})\equiv[N_{\mathbf{k}s}(\mathbf{x}),H^0]/i\hbar=\frac{-i}{2V}\sum_{\mathbf{k}'}(\omega_{\mathbf{k}'s}-\omega_{\mathbf{k}s})\times(a_{\mathbf{k}s}^\dagger a_{\mathbf{k}'s}\exp[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{x}]-\text{H.c.})\times\exp(-\tfrac{1}{4}|\mathbf{k}-\mathbf{k}'|^2l^2). \quad (5.14)$$

It can also be shown that

$$\nabla N_{\mathbf{k}s}(\mathbf{x})=\frac{i}{2V}\sum_{\mathbf{k}'}(\mathbf{k}'-\mathbf{k})\times(a_{\mathbf{k}s}^\dagger a_{\mathbf{k}'s}\exp[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{x}]-\text{H.c.})\times\exp(-\tfrac{1}{4}|\mathbf{k}-\mathbf{k}'|^2l^2). \quad (5.15)$$

The use of these results to evaluate $H^0(\mathbf{x})$ and $\nabla\cdot\mathbf{s}_2^0(\mathbf{x})$ shows that for the conservation equation (2.1) to be satisfied one must have

$$\omega_{\mathbf{k}'s}-\omega_{\mathbf{k}s}=\mathbf{v}_{\mathbf{k}s}\cdot(\mathbf{k}'-\mathbf{k}). \quad (5.16)$$

This condition is certainly satisfied to the approximation being considered, since $\mathbf{v}_{\mathbf{k}s}$ equals $\nabla_{\mathbf{k}}\omega_{\mathbf{k}s}$ and the difference $\mathbf{k}-\mathbf{k}'$ is very small in the region where $\exp(-\frac{1}{4}|\mathbf{k}-\mathbf{k}'|^2l^2)$ is peaked. This verifies the assertion that $\mathbf{s}_2^0(\mathbf{x})$ satisfies a conservation equation in the same approximation that (5.10) is valid.

6. CONCLUSIONS AND DISCUSSION

The expressions for the energy flux, valid for all phases of matter, have been obtained from the requirement that the local flux satisfy a conservation law. With the Hamiltonian expressed as $H=H^0+\lambda H'$, where H^0 is the harmonic Hamiltonian for a lattice, one obtains contributions to the energy flux which are independent of the perturbation $\lambda H'$ and contributions proportional to λ and to λ^2. When expressed in terms of phonons, the perturbation independent part of the average flux separates into

$$\mathbf{S}^0=\mathbf{S}_{2,d}^0+\mathbf{S}_{2,nd}^0+\mathbf{S}_3^0,$$

where $\mathbf{S}_{2,d}^0$ is the diagonal part of $\mathbf{S}^0$ in the phonon representation, $\mathbf{S}_{2,nd}^0$ is nondiagonal and contains contributions from modes with the same wave vector but

different polarization directions, and $\mathbf{S}_3^0$ is a cubic function of the creation and annihilation operators $a_{\mathbf{k}s}^\dagger$ and $a_{\mathbf{k}s}$.

The diagonal part $\mathbf{S}_{2,d}^0$ has the form of the usual expression (1.1) for the lattice energy flux. Diagonal elements in the phonon representation correspond to time-independent terms in the classical harmonic approximation, while nondiagonal terms correspond to oscillatory functions. Thus, when the anharmonic energy is small, one expects the diagonal element to give the major contribution to the (time-averaged) transport of energy.

When one uses the cubic term in the potential energy expansion as a perturbation, its contribution to the flux has the form

$$\lambda\mathbf{S}'=\lambda\mathbf{S}_3'+\lambda\mathbf{S}_4',$$

where $\lambda\mathbf{S}_3'$ and $\lambda\mathbf{S}_4'$ are, respectively, cubic and quartic functions of the operators $a_{\mathbf{k}s}^\dagger$ and $a_{\mathbf{k}s}$. Similarly, an nth power term in the potential energy expansion yields nth and $(n+1)$st power contributions to the flux. Since the product of an even number of creation and annihilation operators can possess diagonal matrix elements, there are in general diagonal contributions to the flux from all powers in the expansion of the Hamiltonian.

Neither $\mathbf{S}_3^0$ nor the $(n+1)$st power contribution from the nth power perturbation would occur, had the energy associated with the various particles been identified with their lattice sites instead of with their actual positions. Because of this one expects these contributions to be significant only when the amplitudes of the particle displacements are appreciable compared to the spacing between particles, such as one anticipates at temperatures near the melting point. Such contributions are, of course, of primary importance when the particle displacements are very large, as in a gas.

It has also been shown that the general expression for the local energy flux $\mathbf{s}(\mathbf{x})$ is given approximately by

$$\mathbf{s}(\mathbf{x})=\sum_{\mathbf{k}s} N_{\mathbf{k}s}(\mathbf{x})\hbar\omega_{\mathbf{k}s}\mathbf{v}_{\mathbf{k}s},$$

where $N_{\mathbf{k}s}(\mathbf{x})$ contains contributions from a packet of normal modes with a spread of wave vectors centered about the value $\mathbf{k}$. To obtain this result it is required that the macroscopically small volume elements over which local properties are averaged be large compared to the interparticle force range and contain many particles.

ACKNOWLEDGMENTS

The author expresses his gratitude to James A. McLennan, who suggested this research, for many illuminating discussions and criticisms. He also thanks William C. Schieve for several helpful comments and suggestions.