Doppler shift in the Mössbauer effect is proportional to the mean-square velocity of the emitting atom. Hence, measurements of this shift provide, in principle, a means of obtaining information about the forces acting on a surface atom compared to those acting on an interior atom. However, technical difficulties associated with preparing samples having the radioactive atoms localized in the surface layers must be surmounted.

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Thermal Conductivity of a System of Interacting Electrons*

J. S. Langer†
University of California, San Diego, La Jolla, California

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Kubo's formula for thermal conductivity is evaluated for the case of an interacting electron gas and random, fixed, impurities. As in previous work, the theorems proved are exact to all orders in the electron-electron interactions and to lowest order in the concentration of impurities. The heat flux is examined in some detail and a Ward's identity is derived for the associated vertex function. Although the heat flux contains contributions from the interaction energy of pairs (or larger clusters) of correlated quasi-particles, it is found that these contributions enter the thermal conductivity only to higher orders in the impurity concentration. In a normal system where the many-body correlations are sufficiently weak, the Wiedemann-Franz law remains valid.

I. INTRODUCTION

The purpose of this paper is to demonstrate that the quasi-particle picture of an interacting Fermi fluid is rigorously applicable to thermal conductivity problems. This picture, originally proposed by Landau,[1] has turned out to be an exact consequence simply of the general structure of many-body perturbation theory. The detailed proof of this fact for various equilibrium properties of the Fermi fluid may be found in a series of papers by Luttinger[2,3]; and a discussion of dc electrical conductivity is contained in previous papers by the present author.[4] In this paper we shall apply the perturbation-theoretic analysis to the calculation of the heat flux associated with a small temperature gradient. In particular, we shall show that the Wiedemann-Franz law remains valid in the presence of interactions between the electrons.

The model to be used here is precisely the same as in the previous work.[4] That is, we consider a system of interacting electrons in the presence of a small concentration of randomly scattered, fixed impurities. The impurities provide the relaxation mechanism for the system. Calculations are performed to all orders in the electron-electron and electron-impurity interactions, and to lowest order in the concentration of impurities.

As a starting point for this calculation we shall use Kubo's formulas for the transport coefficients. Although several steps in the derivation of these formulas are rather subtle and difficult to justify rigorously, we shall proceed on the assumption that the formulas are exact. We define the transport coefficients as follows[5]:

$$\mathbf{j}=-\frac{\mu}{e}L_0\left(\frac{1}{\mu}\nabla\mu-\frac{1}{T}\nabla T\right)-L_1\frac{1}{T}\nabla T;\tag{1.1}$$

$$\mathbf{u}=-\frac{\mu}{e}L_1\left(\frac{1}{\mu}\nabla\mu-\frac{1}{T}\nabla T\right)-L_2\frac{1}{T}\nabla T,\tag{1.2}$$

where $\mathbf{j}$ is the electrical current density and $\mathbf{u}$ is the energy flux. T is the temperature and μ the chemical potential. Then the transport coefficients, L_i, are given by the Kubo formulas[6]:

$$L_0=\frac{1}{3\Omega}\int_0^\infty dt\int_0^\beta d\lambda\ \mathrm{Tr}[\rho_0\mathbf{J}(0)\cdot\mathbf{J}(t+i\lambda)];\tag{1.3}$$

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* Supported in part by the Office of Naval Research.

† National Science Foundation Fellow. Permanent address: Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

[1] L. D. Landau, Sov. Phys.—JETP 3, 920 (1956); 5, 101 (1957).

[2] J. M. Luttinger and J. C. Ward, Phys. Rev. 118, 1417 (1960).

[3] J. M. Luttinger, Phys. Rev. 119, 1153 (1960); 121, 1251 (1961).

[4] J. S. Langer, Phys. Rev. 120, 714 (1960); 124, 1003 (1961); 127, 5 (1962). We shall refer to these papers as I, II, and III, respectively.

[5] For a careful discussion of the definition of the transport coefficients, see H. B. Callen, *Thermodynamics* (John Wiley & Sons, Inc., New York, 1960).

[6] A complete derivation of these formulas may be found in Kubo's lectures at the Summer Institute for Theoretical Physics, University of Colorado, Boulder, 1958. These notes appear in *Lectures in Theoretical Physics* (Interscience Publishers, Inc., New York, 1959), Vol. I. The original papers are R. Kubo, J. Phys. Soc. Japan 12, 570 (1957); R. Kubo, M. Yokota, and S. Nakajima, *ibid.* 12, 1203 (1957). Also see M. I. Klinger, Zhur. Tekh. Fiz. 27, 2780 (1957).

$$L_1=\frac{1}{3\Omega}\int_0^\infty dt\int_0^\beta d\lambda\ \mathrm{Tr}[\rho_0\mathbf{U}(0)\cdot\mathbf{J}(t+i\lambda)]$$

$$=\frac{1}{3\Omega}\int_0^\infty dt\int_0^\beta d\lambda\ \mathrm{Tr}[\rho_0\mathbf{J}(0)\cdot\mathbf{U}(t+i\lambda)];\quad(1.4)$$

$$L_2=\frac{1}{3\Omega}\int_0^\infty dt\int_0^\beta d\lambda\ \mathrm{Tr}[\rho_0\mathbf{U}(0)\cdot\mathbf{U}(t+i\lambda)].\quad(1.5)$$

Here, $\mathbf{J}$ and $\mathbf{U}$ are the Heisenberg operators for the total electrical and energy currents, respectively. ρ_0 is the equilibrium density matrix:

$$\begin{aligned}\rho_0&=(1/Z)\exp[-\beta(H-\mu N)];\\ Z&=\mathrm{Tr}\exp[-\beta(H-\mu N)],\end{aligned}\quad(1.6)$$

where H is the Hamiltonian for the system of electrons and impurities and N is the number operator. $\beta=1/k_BT$, k_B being Boltzmann's constant; and Ω is the volume of the system.

In the absence of a temperature gradient, $\nabla\mu=-e\mathbf{E}$, where $\mathbf{E}$ is the external electric field. Thus, we may identify the dc conductivity σ with L_0:

$$L_0=\sigma.\quad(1.7)$$

The heat flux $\mathbf{q}$ is given by[5]

$$\mathbf{q}=\mathbf{u}-(\mu/e)\mathbf{j}.\quad(1.8)$$

Definition of the thermal conductivity, κ, by

$$\mathbf{q}=-\kappa\nabla T,\quad \mathbf{j}=0,\quad(1.9)$$

leads to

$$\kappa=\frac{1}{T}\left(L_2-\frac{L_1^2}{L_0}\right).\quad(1.10)$$

The major difficulty in the evaluation of the right-hand side of Eq. (1.10) is that, in order to obtain a nonvanishing result, we are required to compute the L's to order T^2. Paper III in this series[4] was devoted to a discussion of how such a calculation must be performed; and we shall use the results of III extensively in the present work. At first glance it would seem that, to order T^2, we should have to include an explicit contribution to the heat flux due to the interaction energy carried by a correlated pair of quasi-particles. In fact, we shall see that such a term does occur; but, as pointed out in III, its contribution to the conductivity does not diverge as the concentration of impurities goes to zero. Roughly speaking, in a normal system the transport associated with a cluster of quasi-particles is limited by the correlation time of the cluster even in the absence of relaxation due to impurity scattering. Thus, as long as the cluster correlation times remain finite—a condition which must be equivalent to "normality"—the independent quasi-particle picture will yield an accurate transport theory.

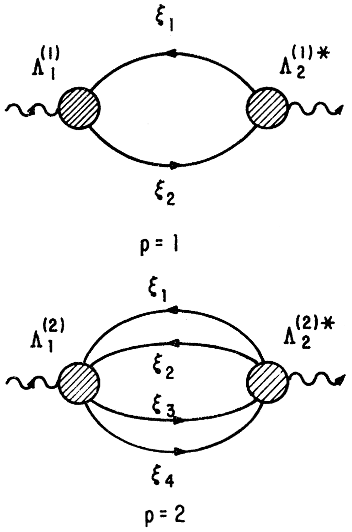

FIG. 1. Reduced diagrams of orders $p=1$ and $p=2$.

The mathematical details of the evaluation of κ are presented here as follows. In Sec. II we review the scheme developed in III for evaluation of the Kubo formulas and indicate the minor modifications which are required when the electric current operator $\mathbf{J}$ is replaced by the energy flux $\mathbf{U}$. The only formal problem not actually solved in III is the proof that the energy flux associated with a single quasi-particle is given by the quasi-particle energy multiplied by the group velocity. This proof is contained in Sec. III of the present paper. Finally, in Sec. IV we exhibit the resulting expression for κ and discuss the Wiedemann-Franz law.

II. GRAPHICAL ANALYSIS

According to the discussion in III, any one of the Kubo formulas (1.3–5) may be evaluated by means of the same perturbation-theoretic techniques as those devised by Luttinger and Ward[2] for the calculation of the Gibbs potential in equilibrium statistical mechanics. In particular, a Kubo formula may be written in terms of the imaginary part of a vacuum-polarization function. A unitarity relation then expresses this imaginary part as a sum over energy-conserving intermediate states. A large section of Paper III was devoted to a demonstration that, for a normal metal, this sum over true intermediate states may be rearranged and labeled according to the number of quasi-particles and quasi-holes which appear as intermediate states in what were referred to as "reduced graphs." The final form of the answer might be said to constitute a "quasi-unitarity" sum. The reader is referred to III for the details of this formulation.

We start now with the sum over reduced graphs as given by Eq. (III 4.6). Some sample reduced diagrams are drawn in Fig. 1. For any one of the transport coefficients, L, we have an expression of the form:

$$L=\frac{\beta\pi}{3\Omega}\sum_{p=1}^{\infty}(-1)^{p+1}\int_{-\infty}^{\infty}d\xi_1\cdots\int_{-\infty}^{\infty}d\xi_{2p}\,\delta(\xi_{2p}+\cdots+\xi_{p+1}-\xi_p-\cdots-\xi_1)f^+(\xi_{2p})\cdots f^+(\xi_{p+1})f^-(\xi_p)\cdots f^-(\xi_1)$$
$$\times\langle\sum_{\gamma}\sum_{\text{mom. spins}}\tfrac{1}{2}(\mathbf{\Lambda}_1{}^{(p)}\cdot\mathbf{\Lambda}_2{}^{(p)*}+\mathbf{\Lambda}_2{}^{(p)}\cdot\mathbf{\Lambda}_1{}^{(p)*})\mathcal{A}(\xi_1)\cdots\mathcal{A}(\xi_{2p})\rangle_{\text{av}}. \quad (2.1)$$

Here, p denotes the order of the reduced graph, i.e., the number of quasi-particle hole pairs which appear. The ξ's play the role of energy variables associated with the $2p$ electron lines (see Fig. 1). The particle or hole nature of each line is indicated by the Fermi functions, $f^{\pm}(\xi)$. Also associated with each explicit line in the reduced graph is the spectral function, $\mathcal{A}(\xi)$. This function is defined to be the discontinuity across the branch cut of the complete single-particle propagator. (It should be emphasized that the propagator referred to here is the analytic continuation of the simple temperature-dependent function used by Luttinger and Ward. It is not the more complicated time and temperature dependent Green's function often used by other authors.) The $\mathbf{\Lambda}^{(p)}$'s are the vertex functions indicated by shaded circles in the diagrams. $\mathbf{\Lambda}^{(p)}$ always is a "proper" vertex function; i.e., no self-energy parts occur on the p ingoing or the p outgoing electron lines. The external interaction line associated with $\mathbf{\Lambda}$ indicates an interaction with either $\mathbf{J}$ or $\mathbf{U}$, depending upon which coefficient L we are dealing with. The sum over γ in Eq. (2.1) indicates that we are to sum over all combinations of vertex diagrams $\mathbf{\Lambda}_1{}^{(p)}\cdot\mathbf{\Lambda}_2{}^{(p)*}$ with the proviso that we never construct a graph in which a self-energy part has been inserted into one of the electron or hole lines which comprise the intermediate state. In other words, if the $\mathbf{\Lambda}^{(p)}$'s are skeleton diagrams, then the entire reduced graph must remain a skeleton diagram. The symmetric form in which the $\mathbf{\Lambda}^{(p)}$'s occur in (2.1) is strictly necessary only for the coefficient L_1, where use of the Onsager symmetry is required in the derivation of this equation. Finally, the angular brackets in (2.1) indicate an average over random configurations of impurities.

The only place in which any of the present analysis might differ from the previous work is the evaluation of those vertex diagrams $\mathbf{\Lambda}^{(p)}$ associated with the energy-flux operator $\mathbf{U}$. In order to complete the graphical analysis, then, we must construct an explicit representation for this operator. We shall not make direct use of this operator in any detailed calculations in this paper; but its general form is important.

Let $\epsilon(\mathbf{x})$ be the energy-density operator at the position $\mathbf{x}$. Then the energy flux is any vector $\mathbf{u}(\mathbf{x})$ which satisfies the conservation law

$$\dot{\epsilon}(\mathbf{x})+\mathbf{\nabla}\cdot\mathbf{u}(\mathbf{x})=0; \quad (2.2)$$

and the total energy flux is

$$\mathbf{U}=\int d^3x\,\mathbf{u}(\mathbf{x}). \quad (2.3)$$

Equation (2.2) defines $\mathbf{u}$ to within a divergenceless vector, which is sufficient for the calculation of the conductivity. Now we know that a vector $\mathbf{u}$ which satisfies (2.2) is given to us automatically by the energy-momentum tensor in the following manner. Consider the Lagrangian

$$L=\int \mathfrak{L}d^3x=-\frac{1}{2m}\int d^3x\,\mathbf{\nabla}\psi^\dagger\cdot\mathbf{\nabla}\psi-\frac{1}{2i}\int d^3x\,(\psi^\dagger\dot{\psi}-\psi\dot{\psi}^\dagger)$$
$$-\frac{1}{2}\int\int d^3x d^3x'\,\psi^\dagger(\mathbf{x})\psi^\dagger(\mathbf{x}')v(\mathbf{x}'-\mathbf{x})\psi(\mathbf{x}')\psi(\mathbf{x}), \quad (2.4)$$

where ψ and $\psi^\dagger$ are to be considered independent Heisenberg operators. The spin dependence of these operators is irrelevant for our purposes and has been omitted. v is the electron-electron interaction potential. To lowest order in the concentration of impurities, the electron-impurity interaction may be omitted in computing the energy flux.

The standard variational procedure applied to (2.4) yields the equation of motion:

$$-\frac{1}{2m}\nabla^2\psi(\mathbf{x})+\int d^3x'\,\psi^\dagger(\mathbf{x}')v(\mathbf{x}'-\mathbf{x})\psi(\mathbf{x}')\psi(\mathbf{x})=i\dot{\psi}(\mathbf{x}), \quad (2.5)$$

and its Hermitian conjugate. Then, the vector $\mathbf{u}$ is given by

$$u_i=\frac{\partial\mathfrak{L}}{\partial(\partial\psi/\partial x_i)}\dot{\psi}+\dot{\psi}^\dagger\frac{\partial\mathfrak{L}}{\partial(\partial\psi^\dagger/\partial x_i)}=-\frac{1}{2m}\left(\frac{\partial\psi^\dagger}{\partial x_i}\dot{\psi}+\dot{\psi}^\dagger\frac{\partial\psi}{\partial x_i}\right)$$
$$=\frac{i}{2m}\frac{\partial\psi^\dagger}{\partial x_i}\left(-\frac{1}{2m}\nabla^2\psi+\int d^3x'\,\psi^\dagger(\mathbf{x}')v(\mathbf{x}'-\mathbf{x})\psi(x')\psi(x)\right)+\text{H.c.}, \quad (2.6)$$

where we have used (2.5) in writing the last line. Direct differentiation of (2.6) verifies Eq. (2.2) with

$$\epsilon(\mathbf{x})=\frac{1}{2m}\nabla\psi^\dagger\cdot\nabla\psi+\frac{1}{2}\int d^3x'\,\psi^\dagger(\mathbf{x})\psi^\dagger(\mathbf{x}')v(\mathbf{x}-\mathbf{x}')\psi(\mathbf{x}')\psi(\mathbf{x}). \tag{2.7}$$

Finally, we transform into momentum space via

$$\psi(\mathbf{x})=\Omega^{-\frac{1}{2}}\sum\nolimits_{\mathbf{k}} a_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{x}}, \tag{2.8}$$

where $a_{\mathbf{k}}$ is the usual annihilation operator for an electron of momentum $\mathbf{k}$. Then we use Eq. (2.3) to find

$$\mathbf{U}=\sum_{\mathbf{k}}\frac{\mathbf{k}}{m}\frac{k^2}{2m}a_{\mathbf{k}}^\dagger a_{\mathbf{k}}+\frac{1}{\Omega}\sum_{\mathbf{k},\mathbf{k}',\mathbf{q}}\frac{1}{2m}(\mathbf{k}+\mathbf{k}')v(\mathbf{q})a_{\mathbf{k}+\mathbf{q}}^\dagger a_{\mathbf{k}'-\mathbf{q}}^\dagger a_{\mathbf{k}'}a_{\mathbf{k}}. \tag{2.9}$$

The first term on the right-hand side of (2.9) is the usual expression for the energy flux associated with noninteracting electrons. The second term is a two-body operator which expresses the contribution of the interaction energy to the total energy flux. The two kinds of elementary vertex diagrams which now must be associated with $\mathbf{U}$ are drawn in Fig. 2. Notice that the two-body vertex leads to diagrams in the evaluation of L_1 and L_2 of quite a different sort than the diagrams which occur in L_0. For example, the graph shown in Fig. 3 has a reduced graph only of order $p=2$; i.e., it makes a contribution to L_2 at most of order T^2.

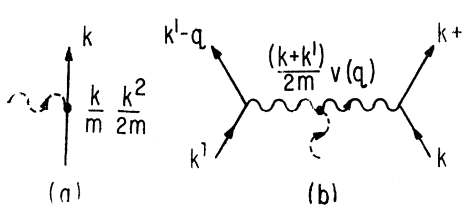

FIG. 2. The two elementary vertex diagrams associated with the energy flux operator $\mathbf{U}$.

III. ENERGY FLUX OF A QUASI-PARTICLE

Having formulated the general rules for the perturbation-theoretic evaluation of the transport coefficients, we turn our attention now to a detailed discussion of the lowest order reduced graph. As pointed out in III, the $p=1$ term in Eq. (2.1) contains the independent quasi-particle model of dc transport processes. The crucial ingredient of this term is the vertex function, $\mathbf{\Lambda}^{(1)}$, which, apart from a normalization factor, is the current associated with a single quasi-particle. For the case of electric current ($\mathbf{J}$) we found previously:

$$\mathbf{\Lambda}_J^{(1)}(\mathbf{k},\xi)=\frac{e\mathbf{k}}{m}-e\frac{\partial}{\partial\mathbf{k}}\Sigma'(\mathbf{k},\xi), \tag{3.1}$$

where Σ' is the proper self-energy function. When $\xi=\xi_{\mathbf{k}}$ such that

$$k^2/2m-\xi_{\mathbf{k}}-\Sigma'(\mathbf{k},\xi_{\mathbf{k}})=0, \tag{3.2}$$

then

$$\mathbf{\Lambda}_J^{(1)}(\mathbf{k},\xi_{\mathbf{k}})=(e/N_{\mathbf{k}})(d\xi_{\mathbf{k}}/d\mathbf{k}), \tag{3.3}$$

where $d\xi_{\mathbf{k}}/d\mathbf{k}$ (or its real part) may be identified as the group velocity of the quasi-particle and

$$N_{\mathbf{k}}^{-1}=1+\left.\frac{\partial\Sigma'(\mathbf{k},\xi)}{\partial\xi}\right|_{\xi=\xi_{\mathbf{k}}} \tag{3.4}$$

is the normalization of the quasi-particle wave function. Thus, the current is given by

$$\mathbf{J}_{\mathbf{k}}=\mathbf{\Lambda}_J^{(1)}(\mathbf{k},\xi_{\mathbf{k}})N_{\mathbf{k}}=e(d\xi_{\mathbf{k}}/d\mathbf{k}), \tag{3.5}$$

i.e., the charge times the group velocity. The purpose of the present section is to derive an analogous expression for the energy flux.

The reader will recall that, although no impurity effects appear explicitly, the impurities played an important role in the derivation of the above formulas. In particular, the presence of the impurities had the mathematical effect of allowing differentiation of the electron propagators with respect to the momentum $\mathbf{k}$, and thus allowed a simple graphical derivation of (3.1). Unfortunately, the operator $\mathbf{U}$ is considerably more complicated than $\mathbf{J}$; and the trick of differentiation does not seem to be applicable. We, therefore, must take a slightly different approach to the evaluation of $\mathbf{\Lambda}_U^{(1)}$.

In preparation for this calculation, let us return to $\mathbf{\Lambda}_J^{(1)}$ and consider the case in which the external interaction line carries a finite momentum and energy, say $\mathbf{q}$ and ν, but there are no impurities in the system. This vertex function is discontinuous at $\mathbf{q}=0$, $\nu=0$. In particular, (see II, Appendix B):

$$\mathbf{\Lambda}_J^{(1)}(\nu=0,\ q\rightarrow 0)=(e/N_{\mathbf{k}})(d\xi_{\mathbf{k}}/d\mathbf{k}); \tag{3.6}$$

but

$$\mathbf{\Lambda}_J^{(1)}(\mathbf{q}=0,\ \nu\rightarrow 0)=(e/m)\mathbf{k}(1/N_{\mathbf{k}}). \tag{3.7}$$

The direct analysis in Paper II indicates that we may get correct results by ignoring the impurities and choosing (3.6) for the vertex function. This choice may

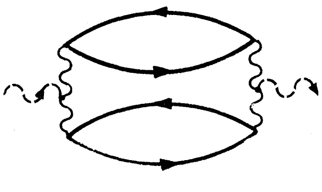

FIG. 3. A diagram contributing to the coefficient L_2.

be further justified by the following intuitive argument. Considered as a function of $\mathbf{q}$, $\mathbf{\Lambda}_J^{(1)}$ is essentially the Fourier transform of the current density associated with a quasi-particle wave packet. We know that this wave packet must be localized within a length of the order of the mean free path, $\lambda \cong (k_F/m)\tau$; thus we must consider q's of the order $\lambda^{-1} \cong m/k_F\tau$. Now the dimensionless ratio which is relevant to the choice between (3.6) and (3.7) is

$$m\nu/qk_F \cong \nu\tau, \qquad (3.8)$$

which must be much less than unity under dc conditions. We conclude that the limits q, $\nu \to 0$ must be taken in the order indicated in Eq. (3.6).

Our procedure now is to compute the energy-flux vertex $\mathbf{\Lambda}_U^{(1)}$ for $\nu = 0$, $q \to 0$ in the absence of impurities. To do this we adopt a technique devised by Takahashi for proving and generalizing the Ward identity in quantum electrodynamics.[7] This technique is based on the observation that the Ward identity [both in electrodynamics and as expressed in Eq. (3.1)] is a direct result of gauge invariance, which, in turn, is equivalent to charge conservation. Thus, Takahashi was able to prove the identity by starting with the charge-current continuity equation. In direct analogy, we use Eq. (2.2) for the starting point of our derivation.

Let $\epsilon(\mathbf{q})$ be the Fourier transform of the energy-density operator given by Eq. (2.7). That is,

$$\epsilon(\mathbf{q}) = \int \epsilon(\mathbf{x}) e^{i\mathbf{q}\cdot\mathbf{x}} d^3x$$

$$= \sum_{\mathbf{k}} \frac{1}{2m} \mathbf{k}\cdot(\mathbf{k}+\mathbf{q}) a_{\mathbf{k}+\mathbf{q}}^\dagger a_{\mathbf{k}} + \tfrac{1}{2} \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}'} \frac{v(\mathbf{q}')}{\Omega} a_{\mathbf{k}+\mathbf{q}'+\mathbf{q}}^\dagger a_{\mathbf{k}'-\mathbf{q}'}^\dagger a_{\mathbf{k}'} a_{\mathbf{k}}. \qquad (3.9)$$

In the formalism of Luttinger and Ward[2] we must consider, instead of the usual Heisenberg operator, the quantity

$$\epsilon(\mathbf{q},\lambda) \equiv e^{\lambda H} \epsilon(\mathbf{q}) e^{-\lambda H}; \qquad (3.10)$$

in which case we have

$$(d/d\lambda)\epsilon(\mathbf{q},\lambda) = -ie^{\lambda H}\dot{\epsilon}(\mathbf{q})e^{-\lambda H} = \mathbf{q}\cdot\mathbf{u}(\mathbf{q},\lambda). \qquad (3.11)$$

Equation (3.11) is the desired form of the energy-conservation equation. Now multiply (3.11) by the modified Heisenberg operators $a_{\mathbf{k}+\mathbf{q}}(\lambda')a_{\mathbf{k}}^\dagger(0)$ and take the λ-ordered satistical average. We find

$$\frac{d}{d\lambda}\langle T[a_{\mathbf{k}+\mathbf{q}}(\lambda')\epsilon(\mathbf{q},\lambda)a_{\mathbf{k}}^\dagger(0)]\rangle$$
$$-\langle T[a_{\mathbf{k}+\mathbf{q}}(\lambda')\mathbf{q}\cdot\mathbf{u}(\mathbf{q},\lambda)a_{\mathbf{k}}^\dagger(0)]\rangle$$
$$=\langle T\{[\epsilon(\mathbf{q},\lambda),a_{\mathbf{k}+\mathbf{q}}(\lambda)]a_{\mathbf{k}}^\dagger(0)\}\rangle\delta(\lambda-\lambda')$$
$$+\langle T\{a_{\mathbf{k}+\mathbf{q}}(\lambda')[\epsilon(\mathbf{q},0),a_{\mathbf{k}}^\dagger(0)]\}\rangle\delta(\lambda). \qquad (3.12)$$

The angular brackets are defined, for any operator A, by

$$\langle A\rangle \equiv \mathrm{Tr}\rho_0 A. \qquad (3.13)$$

The two terms on the right-hand side of (3.12) occur because we have taken $d/d\lambda$ outside of the quantity subject to the T operation.

The next step is to compute the Fourier coefficients of Eq. (3.12) via the operation

$$\int_0^\beta d\lambda' \int_0^\beta d\lambda\, e^{\zeta_l\lambda'} e^{\nu_m(\lambda'-\lambda)}\cdots;$$

$$\zeta_l = \mu + (\pi i/\beta)(2l+1); \quad \nu_m = 2\pi i m/\beta. \qquad (3.14)$$

In accord with the above discussion, we may immediately set $\nu_m = 0$. The resulting equation is

$$-S'(\mathbf{k}+\mathbf{q},\zeta_l)\mathbf{q}\cdot\mathbf{\Lambda}_U^{(1)}S'(\mathbf{k},\zeta_l)$$
$$=\int_0^\beta d\lambda\, e^{\zeta_l\lambda}\langle T\{[\epsilon(\mathbf{q},\lambda),a_{\mathbf{k}+\mathbf{q}}(\lambda)]a_{\mathbf{k}}^\dagger(0)\}\rangle$$
$$+\int_0^\beta d\lambda\, e^{\zeta_l\lambda}\langle T\{a_{\mathbf{k}+\mathbf{q}}(\lambda)[\epsilon(\mathbf{q},0),a_{\mathbf{k}}^\dagger(0)]\}\rangle. \qquad (3.15)$$

The left-hand side of (3.15) has been obtained by means of the usual diagrammatic interpretation of the λ-dependent expectation value which occurs in (3.12). In this way we have passed from the energy-conservation equation to a relation which contains the desired vertex function $\mathbf{\Lambda}_U^{(1)}$.

It remains to find a diagrammatic interpretation of the right-hand side of (3.15). The commutators which appear there are

$$[\epsilon(\mathbf{q}),a_{\mathbf{k}+\mathbf{q}}] = -\frac{1}{2m}\mathbf{k}\cdot(\mathbf{k}+\mathbf{q})a_{\mathbf{k}} - A - B; \qquad (3.16)$$

$$A = \tfrac{1}{2}\sum_{\mathbf{k}',\mathbf{q}'}\frac{v(\mathbf{q}')}{\Omega}a_{\mathbf{k}'+\mathbf{q}'+\mathbf{q}}^\dagger a_{\mathbf{k}'}a_{\mathbf{k}+\mathbf{q}+\mathbf{q}'}; \qquad (3.17)$$

$$B = \tfrac{1}{2}\sum_{\mathbf{k}',\mathbf{q}'}\frac{v(\mathbf{q}')}{\Omega}a_{\mathbf{k}'+\mathbf{q}'}^\dagger a_{\mathbf{k}'}a_{\mathbf{k}+\mathbf{q}'}; \qquad (3.18)$$

$$[\epsilon(\mathbf{q}),a_{\mathbf{k}}^\dagger] = \frac{1}{2m}\mathbf{k}\cdot(\mathbf{k}+\mathbf{q})a_{\mathbf{k}+\mathbf{q}}^\dagger + C + D; \qquad (3.19)$$

$$C = \tfrac{1}{2}\sum_{\mathbf{k}',\mathbf{q}'}\frac{v(\mathbf{q}')}{\Omega}a_{\mathbf{k}+\mathbf{q}'}^\dagger a_{\mathbf{k}'-\mathbf{q}'+\mathbf{q}}^\dagger a_{\mathbf{k}'}; \qquad (3.20)$$

$$D = \tfrac{1}{2}\sum_{\mathbf{k}',\mathbf{q}'}\frac{v(\mathbf{q}')}{\Omega}a_{\mathbf{k}+\mathbf{q}+\mathbf{q}'}^\dagger a_{\mathbf{k}'-\mathbf{q}'}^\dagger a_{\mathbf{k}'}. \qquad (3.21)$$

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[7] Y. Takahashi, Nuovo cimento **7**, 371 (1957).

The first terms in (3.16) and (3.19), i.e., the kinetic energy terms, may be inserted into (3.15) to give

$$-\frac{1}{2m}\mathbf{k}\cdot(\mathbf{k}+\mathbf{q})\int_0^\beta d\lambda\, e^{\zeta_l\lambda}\langle T\{a_{\mathbf{k}}(\lambda)a_{\mathbf{k}}^\dagger(0)\}\rangle=-\frac{1}{2m}\mathbf{k}\cdot(\mathbf{k}+\mathbf{q})S'(\mathbf{k},\zeta_l);\tag{3.22}$$

and

$$\frac{1}{2m}\mathbf{k}\cdot(\mathbf{k}+\mathbf{q})\int_0^\beta d\lambda\, e^{\zeta_l\lambda}\langle T\{a_{\mathbf{k}+\mathbf{q}}(\lambda)a_{\mathbf{k}+\mathbf{q}}^\dagger(0)\}\rangle=\frac{1}{2m}\mathbf{k}\cdot(\mathbf{k}+\mathbf{q})S'(\mathbf{k}+\mathbf{q},\zeta_l).\tag{3.23}$$

The interaction terms A through D are slightly more difficult, however. By suitably relabeling the variables of summation, we may rewrite (3.17) and (3.20):

$$\begin{aligned}A&=B+\tfrac{1}{2}\sum_{\mathbf{q}',\mathbf{k}'}\frac{1}{\Omega}[v(\mathbf{q}'-\mathbf{q})-v(\mathbf{q}')]a_{\mathbf{k}'+\mathbf{q}'}^\dagger a_{\mathbf{k}'}a_{\mathbf{k}+\mathbf{q}'}\\&\cong B-\frac{1}{2\Omega}\sum_{\mathbf{k}',\mathbf{q}'}\mathbf{q}\cdot\frac{\partial v}{\partial\mathbf{q}'}a_{\mathbf{k}'+\mathbf{q}'}^\dagger a_{\mathbf{k}'}a_{\mathbf{k}+\mathbf{q}'};\end{aligned}\tag{3.24}$$

and

$$\begin{aligned}C&=D+\frac{1}{2\Omega}\sum_{\mathbf{k}',\mathbf{q}'}[v(\mathbf{q}'+\mathbf{q})-v(\mathbf{q}')]a_{\mathbf{k}+\mathbf{q}'+\mathbf{q}}^\dagger a_{\mathbf{k}'-\mathbf{q}'}^\dagger a_{\mathbf{k}'}\\&\cong D+\frac{1}{2\Omega}\sum_{\mathbf{k}',\mathbf{q}'}\mathbf{q}\cdot\frac{\partial v}{\partial\mathbf{q}'}a_{\mathbf{k}+\mathbf{q}'+\mathbf{q}}^\dagger a_{\mathbf{k}'-\mathbf{q}'}^\dagger a_{\mathbf{k}'}.\end{aligned}\tag{3.25}$$

The operators B and D are illustrated graphically in Fig. 4. The correction terms, $A-B$ and $C-D$, may be interpreted similarly except that, to first order in $\mathbf{q}$, we must replace $v(\mathbf{q}')$ by $\mathbf{q}\cdot\partial v/\partial\mathbf{q}'$. Now we may identify

$$-\int_0^\beta d\lambda e^{\zeta_l\lambda}\langle T[2B(\lambda)a_{\mathbf{k}}^\dagger(0)]\rangle=-\Sigma'(\mathbf{k},\zeta_l)S'(\mathbf{k},\zeta_l);\tag{3.26}$$

and

$$\int_0^\beta d\lambda e^{\zeta_l\lambda}\langle T[a_{\mathbf{k}+\mathbf{q}}(\lambda)2D(0)]\rangle=S'(\mathbf{k}+\mathbf{q},\zeta_l)\Sigma'(\mathbf{k}+\mathbf{q},\zeta_l).\tag{3.27}$$

Exactly the same equations pertain for the correction terms except that we must replace Σ by, say, $\mathbf{q}\cdot\mathbf{\Pi}$ where $\mathbf{q}\cdot\mathbf{\Pi}$ is obtained by replacing the first interaction $v(\mathbf{q}')$ in Σ by $\mathbf{q}\cdot\partial v/\partial\mathbf{q}'$. Notice, however, that the sign of this term is different in Eqs. (3.24) and (3.25).

The resulting form of Eq. (3.15) is

$$\begin{aligned}-S'(\mathbf{k}+\mathbf{q},\zeta_l)\mathbf{q}\cdot\mathbf{\Lambda}_U{}^{(1)}S'(\mathbf{k},\zeta_l)={}&\frac{1}{2m}\mathbf{k}\cdot(\mathbf{k}+\mathbf{q})[S'(\mathbf{k}+\mathbf{q},\zeta_l)-S'(\mathbf{k},\zeta_l)]+S'(\mathbf{k}+\mathbf{q},\zeta_l)\Sigma'(\mathbf{k}+\mathbf{q},\zeta_l)-\Sigma'(\mathbf{k},\zeta_l)S'(\mathbf{k},\zeta_l)\\&+\tfrac{1}{2}S'(\mathbf{k}+\mathbf{q},\zeta_l)\mathbf{q}\cdot\mathbf{\Pi}(\mathbf{k}+\mathbf{q},\zeta_l)+\tfrac{1}{2}\mathbf{q}\cdot\mathbf{\Pi}(\mathbf{k},\zeta_l)S'(\mathbf{k},\zeta_l).\end{aligned}\tag{3.28}$$

This equation may be solved easily for $\mathbf{q}\cdot\mathbf{\Lambda}_U{}^{(1)}$. We use the relation

$$S'(\mathbf{k},\zeta_l)=\frac{1}{k^2/2m-\zeta_l-\Sigma'(\mathbf{k},\zeta_l)},\tag{3.29}$$

and keep only terms to first order in $\mathbf{q}$. Then

$$\begin{aligned}\mathbf{q}\cdot\mathbf{\Lambda}_U{}^{(1)}(\mathbf{k},\zeta_l)={}&\zeta_l\mathbf{q}\cdot\left(\frac{\mathbf{k}}{m}-\frac{\partial}{\partial\mathbf{k}}\Sigma'(\mathbf{k},\zeta_l)\right)\\&+\mathbf{q}\cdot\left(\frac{\mathbf{k}}{m}+\mathbf{\Pi}(\mathbf{k},\zeta_l)\right)\left(\frac{k^2}{2m}-\zeta_l-\Sigma'(\mathbf{k},\zeta_l)\right).\end{aligned}\tag{3.30}$$

Finally, let $\mathbf{q}$ go to zero and analytically continue ζ_l to real ξ as discussed in III. We have

$$\begin{aligned}\mathbf{\Lambda}_U{}^{(1)}(\mathbf{k},\xi)={}&\xi\left(\frac{\mathbf{k}}{m}-\frac{\partial}{\partial\mathbf{k}}\Sigma'(\mathbf{k},\xi)\right)\\&+\left(\frac{\mathbf{k}}{m}+\mathbf{\Pi}(\mathbf{k},\xi)\right)\left(\frac{k^2}{2m}-\xi-\Sigma'(\mathbf{k},\xi)\right).\end{aligned}\tag{3.31}$$

This is the desired analog of Eq. (3.1).

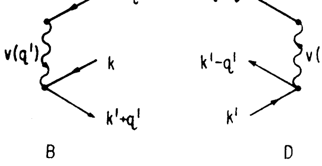

FIG. 4. Diagrammatic interpretation of the operators B and D appearing in Eqs. (3.18) and (3.21).

Notice the following properties of Eq. (3.31). If the electron-electron interaction vanishes, then

$$\mathbf{\Lambda}_U^{(1)}(\mathbf{k},\xi)=(\mathbf{k}/m)(k^2/2m),\qquad(3.32)$$

which is the correct energy flux for a free electron, i.e., the vertex drawn in Fig. 2(a). For a real quasi-particle, on the other hand, $\xi=\xi_{\mathbf{k}}$ according to Eq. (3.2) and the complicated second term in (3.31) vanishes. In this case,

$$\mathbf{U}_{\mathbf{k}}=\mathbf{\Lambda}_U^{(1)}(\mathbf{k},\xi_{\mathbf{k}})N_{\mathbf{k}}=\xi_{\mathbf{k}}(d\xi_{\mathbf{k}}/d\mathbf{k});\qquad(3.33)$$

i.e., the energy flux is equal to the energy $\xi_{\mathbf{k}}$ times the group velocity $d\xi_{\mathbf{k}}/d\mathbf{k}$.

IV. THE WIEDEMANN-FRANZ LAW

It is now a fairly simple matter to deduce the Wiedemann-Franz law. In the standard treatment of the transport coefficients, the quantities L_i may be written in the form:

$$L_i=-\frac{1}{e^i}\int_{-\infty}^{\infty}\frac{df^-(\xi)}{d\xi}\xi^i\sigma(\xi)d\xi,\quad i=0,1,2.\qquad(4.1)$$

Then the electrical conductivity is $\sigma=\sigma(\mu)$; and the thermal conductivity κ turns out to be

$$\kappa=\pi^2k_B{}^2T\sigma/3e^2.\qquad(4.2)$$

Equation (4.2) is obtained by expanding (4.1) to order T^2 and using Eq. (1.10). It follows that, in order to prove the Wiedemann-Franz law (4.2), we need only show that, to order T^2, the L_i may be written in the form (4.1).

Recall first some results of the analysis described in Paper III. Near zero temperature, a reduced graph of order p was found to behave like $T^{2(p-1)}$. Thus, to order T^2 we need consider reduced graphs of order $p=1$ and $p=2$. For $p=1$ we have from (2.1):

$$L^{(1)}=\frac{\beta\pi}{3\Omega}\int_{-\infty}^{\infty}d\xi\, f^+(\xi)f^-(\xi)\times\Big\langle\sum_{\text{mom. spins}}\mathrm{Re}(\mathbf{\Lambda}_1{}^{(1)}\cdot\mathbf{\Lambda}_2{}^{(1)*})\mathcal{A}(\xi)\mathcal{A}(\xi)\Big\rangle_{\text{av}}.\qquad(4.3)$$

Here, we have summed over all proper vertex functions $\mathbf{\Lambda}$; and the subscripts 1, 2 serve only to remind us that we must insert $\mathbf{\Lambda}_J$ or $\mathbf{\Lambda}_U$ depending upon which of the L's we are calculating. Next, to lowest order in the concentration of impurities, we may write

$$L^{(1)}=\frac{\beta\pi}{3\Omega}\int_{-\infty}^{\infty}d\xi f^+(\xi)f^-(\xi)\sum_{\text{mom. spins}}\mathrm{Re}(\mathbf{\Lambda}_1{}^{(1)}\cdot\mathbf{\Lambda}_2{}^{(1)*})\frac{1}{2\pi}\frac{1}{\Gamma_{\text{imp}}+\Gamma_e(\mathbf{k},\xi)}\delta\left[\frac{k^2}{2m}-\xi-\Delta'(\mathbf{k},\xi)\right].\qquad(4.4)$$

Δ' and Γ_e are the real and imaginary parts, respectively, of the electron self-energy function computed in the absence of impurities. All of the impurity effects are contained in Γ_{imp} which may be written in the form

$$\Gamma_{\text{imp}}(\mathbf{k},\ \xi=\xi_{\mathbf{k}})=\frac{n_i}{2N_{\mathbf{k}}}\frac{d\xi_{\mathbf{k}}}{dk}\int_0^{\pi}\sigma(k,\theta)(1-\cos\theta)2\pi\sin\theta d\theta=\frac{1}{2N_{\mathbf{k}}\tau_{\mathbf{k}}}.\qquad(4.5)$$

Here, $\sigma(k,\theta)$ is the differential cross section for scattering of a single quasi-particle by an isolated impurity. $\tau_{\mathbf{k}}$ is the associated relaxation time. The derivation of (4.5) may be found in I, Sec. VIII, and II, Sec. III A.

Γ_e is of order T^2; thus, for our purposes we may approximate

$$\frac{1}{\Gamma_e+\Gamma_{\text{imp}}}\cong\frac{1}{\Gamma_{\text{imp}}}-\frac{\Gamma_e}{\Gamma_{\text{imp}}{}^2}.\qquad(4.6)$$

It was shown in III that the second term on the right-hand side of (4.6) cancels against a class of diagrams of order $p=2$. We know *a priori* that this cancellation must occur because the presence of Γ_e in the denominator in (4.4) would imply a current relaxation via electron-electron collisions. The desired cancellation follows from the fact that electric current is conserved in such collisions. [See Eq. (5.19) in III.] The same argument applies to the energy flux despite the fact that energy flux is not generally conserved in collisions. To order T^2 the scattering events are confined to the Fermi surface, and energy flux is conserved in an elastic collision between two particles of the same energy. The remaining terms of order $p=2$ were shown in III to be negligibly small in the sense that they remain finite in the limit of vanishing impurity concentration.

We now have

$$L=-\frac{1}{3\Omega}\int_{-\infty}^{\infty}\frac{df^-}{d\xi}\sum_{\mathbf{k}}\mathrm{Re}(\mathbf{\Lambda}_1{}^{(1)}\cdot\mathbf{\Lambda}_2{}^{(1)*})\times\frac{1}{\Gamma_{\text{imp}}(\mathbf{k},\xi)}\delta\left[\frac{k^2}{2m}-\xi-\Delta'(\mathbf{k},\xi)\right].\qquad(4.7)$$

The spin sum has been replaced by a factor 2. Referring to the expression for the energy-flux vertex given in Eq. (3.31), we see that we may write

$$\mathbf{\Lambda}_U(\mathbf{k},\xi)=(\xi/e)\mathbf{\Lambda}_J(\mathbf{k},\xi),\qquad(4.8)$$

by virtue of the delta function which appears in (4.7). Again we have made approximations to order T^2; i.e., we have neglected the imaginary parts of Σ' and $\mathbf{\Pi}$. Notice that, in the case of L_1 taking the real part of the combination of vertex functions is absolutely essential at this point. We have now proven Eq. (4.1) by explicit construction of the function $\sigma(\xi)$:

$$\sigma(\xi)=\frac{1}{3\Omega}\sum_{\mathbf{k}}|\mathbf{\Lambda}_J(\mathbf{k},\xi)|^2 \times\frac{1}{\Gamma_{\mathrm{imp}}(\mathbf{k},\xi)}\delta\left[\frac{k^2}{2m}-\xi-\Delta'(\mathbf{k},\xi)\right]. \qquad (4.9)$$

As mentioned above, the Wiedemann-Franz law follows immediately.

It should be emphasized that the Wiedemann-Franz law has been proved here only in the limit of zero temperature and very small concentration of impurities. The important criterion is that the relaxation time associated with impurity scattering be much longer than the correlation time for any cluster of quasi-particles. This consideration makes it seem unlikely that the law is of any more general validity.[8] For example, we have seen that to the next higher order in the impurity concentration, i.e., the zeroth order, we must include in the heat flux the correlation energy carried by a pair of interacting quasi-particles. No analogous term occurs in the electrical conductivity; thus, it seems that the Wiedemann-Franz law must fail when the impurities become sufficiently dense or the many-body correlations sufficiently strong.

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[8] G. V. Chester and A. Thellung [Proc. Phys. Soc. (London), **77**, 1005 (1961)] have shown that, in the case of noninteracting electrons, the Wiedemann-Franz law is correct for all concentrations of impurities. Apparently introduction of the electron-electron interactions destroys this result.