

## DOUBLE-TIME GREEN FUNCTIONS IN STATISTICAL PHYSICS

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## 1. INTRODUCTION

THE methods of modern quantum field theory have recently more and more penetrated into statistical physics. This is connected with the fact that the basic problems in both fields are very much the same. The problem of a particle interacting with a quantized field, or that of a system of interacting fields, is formulated in terms of second-quantized Hamiltonians (or Lagrangians) just as the basic problem of statistical mechanics, that of a system of interacting particles. The peculiar nature of statistical mechanics consists in that we are dealing there with "large" systems with a very large number of particles, and are interested only in the asymptotic properties of such systems for which the number of particles  $N$  tends to infinity (while  $V/N = \text{const}$ , where  $V$  is the volume of the system). This introduces peculiar difficulties when one wants to apply perturbation theory in statistical mechanics, as the perturbation operators are not small and can lead to terms proportional to powers of the volume  $V$  which must, of course, cancel one another in the final result. These difficulties have comparatively recently been solved by the creation of a regularized perturbation theory for large systems, by means of expansions in connected diagrams. Such a theory has been developed both for the zero temperature case (Van Hove<sup>1</sup>, Goldstone<sup>2</sup>, and Hugenholtz<sup>3</sup>), and for the non-vanishing temperature case (Dyson<sup>4</sup>, Bloch, and De Dominicis<sup>5</sup>).

It is characteristic of the systems studied in statistical mechanics that their energy levels are very dense so that the distance between them tends to zero as  $V \rightarrow \infty$ . The spectrum is thus practically continuous and the perturbation energy is always larger than the distance between the levels. One must in that case, strictly speaking, use perturbation theory for the con-

tinuous spectrum. It is therefore particularly important here to work out methods which are not directly based upon perturbation theory.

One of the important concepts of quantum field theory is that of the Green functions, which are convenient for the study of the properties of interacting quantized fields.<sup>6</sup> The use of these concepts turns out to be useful also in statistical mechanics. The application of Green functions makes it possible, for instance, to obtain for the energy regularized expansions which do not contain higher powers of the volume; (cf. Klein and Prange<sup>7</sup>) and in this way there is no difficulty in applying perturbation theory to large systems. The application of Green functions turns out to be useful in those cases where one can sum some type of perturbation-theory diagrams. Tasks of this kind are performed more simply with Green functions.

The application of Green functions is particularly fruitful in the quantum theory of fields when combined with spectral representations of the kind of the Lehmann-Källén relations.<sup>8</sup> Spectral representations for the time-correlation functions and for retarded Green functions were first established and used in statistical mechanics in the theory of fluctuations and in the statistical mechanics of irreversible processes, beginning with a paper by Callen and Welton<sup>9</sup> (see Kubo's paper<sup>10</sup>).

The spectral theorems for the causal time-dependent Green functions were considered in reference 11 for zero temperature and in reference 12 for non-vanishing temperatures, and were used for different problems of statistical mechanics in references 11a-18, 51-52, 7, and 61.

In the present paper we shall not discuss all papers on the application of Green functions in statistical physics, and we refer the reader to the references

given (see also references 50, 53, 54, and 66-69). We shall, however, discuss at greater length one aspect which seems to us to be very promising, namely, the application of double-time temperature-dependent (retarded and advanced) Green functions. We shall give a brief account of the basic properties of the temperature-dependent double-time Green functions (Secs. 2 and 3) and their simplest applications to the theory of irreversible processes (Sec. 4), to the theory of superconductivity (Sec. 6), to ferromagnetism (Sec. 7), and to a system of electrons interacting with the lattice in normal metals and semiconductors (Sec. 8). In the applications we shall follow Bogolyubov and Tyablikov<sup>19</sup> and use not the causal Green functions, as is usually done, but the double-time retarded and advanced Green functions. We shall show that they are very convenient for applications in statistics as they can be analytically continued in the complex plane. Sometimes one uses also in statistical mechanics Matsubara's temperature-dependent Green functions,<sup>20</sup> which are independent of the time, but they are apparently less convenient than the temperature- and time-dependent Green functions.

## 2. DOUBLE-TIME TEMPERATURE-DEPENDENT GREEN FUNCTIONS

### 2.1 Causal, Retarded, and Advanced Green Functions

The Green functions in statistical mechanics are the appropriate generalization of the concept of correlation functions. They are just as intimately connected with the evaluation of observed quantities and they have well-known advantages when equations are formulated and solved.

We can consider in statistical mechanics, as in the quantum theory of fields, different kinds of Green functions, for instance: the double-time causal Green function  $G_C(t, t')$ , defined in terms of the average value of the T product of operators, or the retarded and advanced Green functions  $G_R(t, t')$  and  $G_A(t, t')$

$$G_C(t, t') = \ll A(t); B(t') \gg_c = -i \langle TA(t)B(t') \rangle, \quad (2.1a)$$

$$G_R(t, t') = \ll A(t); B(t') \gg_r = -i\theta(t-t') \langle [A(t), B(t')] \rangle, \quad (2.1b)$$

$$G_A(t, t') = \ll A(t); B(t') \gg_a = i\theta(t'-t) \langle [A(t), B(t')] \rangle, \quad (2.1c)$$

where  $\langle \dots \rangle$  indicates that one should average over a grand canonical ensemble, and where  $\ll A(t)B(t') \gg_{c,r,a}$  are abbreviated notations for the corresponding Green functions.

$$\langle \dots \rangle = Q^{-1} \text{Sp} \left( e^{-\frac{\mathcal{H}}{\theta}} \dots \right) \quad (\theta = kT), \quad (2.2)$$

$$Q = \text{Sp} \left( e^{-\frac{\mathcal{H}}{\theta}} \right) = e^{-\frac{\Omega}{\theta}} \quad (2.3)$$

( $Q$  is the partition function for the grand ensemble, and  $\Omega$  the thermodynamic potential of the variables

$V$ ,  $\theta$ , and  $\mu$ ). The operator  $\mathcal{H}$  includes a term with the chemical potential  $\mu$

$$\mathcal{H} = H - \mu N. \quad (2.4)$$

$H$  is the time-independent Hamiltonian operator and  $N$  the operator of the total number of particles;  $A(t)$ , and  $B(t)$  are the Heisenberg representations of the operators  $A$  and  $B$ , expressed in terms of a product of quantized field functions (or of particle creation and annihilation operators)\*

$$A(t) = e^{i\mathcal{H}t} A e^{-i\mathcal{H}t} \quad (2.5)$$

(a system of units in which  $\hbar = 1$  is used throughout).

The symbol T indicates the time-ordered or T product of operators, which is defined in the usual way

$$TA(t)B(t') = \theta(t-t')A(t)B(t') + \eta\theta(t'-t)B(t')A(t), \quad (2.6)$$

where

$$\theta(t) = \begin{cases} 1 & t > 0 \\ 0 & t < 0, \end{cases} \quad \eta = \pm 1$$

Finally,  $[A, B]$  indicates the commutator or anti-commutator

$$[A, B] = AB - \eta BA, \quad \eta = \pm 1. \quad (2.7)$$

The sign of  $\eta$  in (2.6) and (2.7) is chosen positive or negative by considering what is most convenient for the problem. One usually chooses the positive sign, if  $A$  and  $B$  are Bose operators, and the negative sign if they are Fermi operators, but the other choice of the sign of  $\eta$  is also possible. Generally speaking,  $A$  and  $B$  are neither Bose nor Fermi operators, for products of operators can satisfy more complicated commutation relations. The sign of  $\eta$  for multiple-time Green functions is usually determined uniquely, depending on whether an odd or even permutation of the Fermi operators in these functions is involved in going over to the chronological order [see (2.13)].

We use (2.6) and (2.7) to write (2.1a, b, and c) in the form

$$G_C(t, t') = -i\theta(t-t') \langle A(t)B(t') \rangle - i\eta\theta(t'-t) \langle B(t')A(t) \rangle, \quad (2.8a)$$

$$G_R(t, t') = -i\theta(t-t') \{ \langle A(t)B(t') \rangle - \eta \langle B(t')A(t) \rangle \}, \quad (2.8b)$$

$$G_A(t, t') = i\theta(t'-t) \{ \langle A(t)B(t') \rangle - \eta \langle B(t')A(t) \rangle \}, \quad (\eta = \pm 1). \quad (2.8c)$$

We note that when the time arguments are the same,  $t = t'$ , the Green functions (2.8) are not defined because of the discontinuous factor  $\theta(t-t')$ . This indeterminacy is well known from the quantum theory of fields.

From the definition (2.1) or (2.8) we see that the Green functions applied in statistics differ from the

\*Green functions constructed from operators in the Heisenberg representation with  $\mathcal{H} = H - \mu N$  were applied in references 51, 18, and 19.

field-theoretical Green functions only in the way the averages are taken. Instead of averaging over the lowest (vacuum) state of the system, one averages over the grand canonical ensemble (2.2). The Green functions in statistics depend therefore not only on the time, but also on the temperature. It is clear that when the temperature tends to zero the Green functions (2.1) go over into the usual field-theoretical Green functions.

The application of the grand ensemble is not accidental. It is very convenient, for when it is used no additional limitation on the constancy of the total number of particles need be taken into account, as one must do, for instance, in the canonical ensemble, and the occupation numbers of the different states are independent.

We note that in the case of statistical equilibrium the Green functions  $G_C(t, t')$ ,  $G_R(t, t')$ , and  $G_A(t, t')$  depend on  $t$  and  $t'$  only through  $(t-t')$ . Let us consider  $G_C(t, t')$ , for instance, and write it in explicit form, using the commutability of the operators under the Sp sign

$$G_C(t, t') = -i\theta(t-t')Q^{-1}\text{Sp}\{e^{\mathcal{E}\theta}[i(t-t')-\beta]_A e^{-i\mathcal{E}\theta(t-t')}B\} \\ -i\eta\theta(t'-t)Q^{-1}\text{Sp}\{e^{\mathcal{E}\theta}[i(t'-t)-\beta]_B e^{i\mathcal{E}\theta(t'-t)}A\} \left(\beta = \frac{1}{\theta}\right). \quad (2.9)$$

$G_C(t, t')$  depends thus, indeed, only on  $t-t'$ . We can likewise verify that  $G_R(t, t')$  and  $G_A(t, t')$  depend only on  $t-t'$

$$G_C(t, t') = G_C(t-t'), \quad G_R(t, t') \\ = G_R(t-t'), \quad G_A(t, t') = G_A(t-t'). \quad (2.10)$$

For the time being we introduced the Green functions (2.1) purely formally, by analogy with the quantum theory of fields. We shall satisfy ourselves now by concrete examples that they are very conveniently applied in quantum statistics to problems concerning a system of a large number of interacting particles. One can choose for the operators  $A$  and  $B$  operators of different kinds: for instance, Fermi or Bose operators and their products (Secs. 6 and 8), Pauli operators and their products (Sec. 7), density operators, or current operators (Secs. 4 and 8). The choice of the operators  $A$  and  $B$  is determined by the conditions of the problem.

The Green functions (2.1) are double-time Green functions, in contradistinction to the causal multiple-time Green functions

$$G_C(x_1, t_1, \dots, x_n, t_n; x'_1, t'_1, \dots, x'_n, t'_n) \\ = \langle i \rangle^n \langle T\psi(x_1, t_1), \dots, \psi(x_n, t_n)\psi^*(x'_1, t'_1), \dots, \psi^*(x'_n, t'_n) \rangle, \quad (2.11)$$

where  $\psi(x, t)$  and  $\psi^*(x, t)$  are second quantized field functions in the Heisenberg representation

$$\left. \begin{aligned} \psi(x, t) &= \sum_f a_f(t) \varphi_f(x), \\ \psi^*(x, t) &= \sum_f a_f^*(t) \varphi_f^*(x), \end{aligned} \right\} \quad (2.12)$$

$a_f, a_f^\dagger$  are the annihilation and creation operators (Fermi or Bose operators),  $\varphi_f(x)$  is a complete orthogonal set of one-particle functions, normalized in some volume  $V$ , for instance,  $\varphi_f(x) = V^{-\frac{1}{2}} e^{i f x}$  for spinless particles, where  $f$  is the momentum; for particles with spin  $f = (f, \sigma)$  indicates both the momentum and the spin. The time-ordered or  $T$  product of  $n$  operators  $A_1(x_1), \dots, A_n(x_n)$  is defined as usual as their product in chronological order, multiplied by  $\eta = (-1)^P$ , where  $P$  is the parity of the permutation of the Fermi operators when we change from the order  $1, 2, \dots, n$  to the chronological order

$$T(A_1(x_1), \dots, A_n(x_n)) = \eta A_{j_1}(x_{j_1}), \dots, A_{j_n}(x_{j_n}) \\ t_{j_1} > t_{j_2} > \dots > t_{j_n}. \quad (2.13)$$

$x_j = (x_j, t_j)$  is a point in space-time.

Multiple-time causal Green functions of the kind (2.11) are well known in the quantum theory of fields, where the averaging is over the "vacuum."

We note that the coordinates and the time occur symmetrically in the multiple-time Green functions. This is not essential for statistical mechanics. Here the application of the double-time Green functions (2.1) is the most convenient, since we can use for them spectral expansions which greatly facilitate the solution of the equations for the Green functions. On the other hand, the double-time Green functions contain sufficiently complete information about the properties of a many-particle system so that one can handle most problems in statistical mechanics by applying double-time Green functions. The most convenient double-time Green functions in statistical mechanics are the retarded and advanced Green functions  $G_R$  and  $G_A$ .<sup>19</sup> It follows from the definition (2.8b,c) that  $G_R(t-t')$  vanishes for  $t < t'$ , and  $G_A(t-t')$  for  $t > t'$ . We shall see in the following that the advantage of the functions  $G_R$  and  $G_A$  lies in the fact that they can be continued analytically in the complex plane (Sec. 3).

## 2.2 Equations for Green Functions

We shall obtain a set of equations for the Green functions (2.1). The operators  $A(t)$  and  $B(t)$  satisfy equations of motion of the form

$$i \frac{dA}{dt} = AH - HA. \quad (2.14)$$

The right hand side of (2.14) can be written in more detail using the explicit form of the Hamiltonian and the commutation relations for the operators. Differentiating the Green functions (2.1a, b, and c) with respect to  $t$  we get the equation

$$i \frac{dG}{dt} = i \frac{d}{dt} \langle A; B \rangle = \frac{d\theta(t-t')}{dt} \langle [A(t), B(t')] \rangle \\ + \langle i \frac{dA(t)}{dt}; B(t') \rangle, \quad (2.15)$$

which is the same for all three Green functions  $G_C$ ,  $G_R$ , and  $G_A$ , since  $d\theta(-t)/dt = -d\theta(t)/dt$ ; we shall

therefore simply write  $G$  and  $\ll \dots \gg$  without indices. Taking furthermore into account the relation between the discontinuous function  $\theta(t)$  and the  $\delta$  function of  $t$

$$\theta(t) = \int_{-\infty}^t \delta(t) dt \quad (2.16)$$

and the equations of motion (2.14) for the operator  $A(t)$ , we can write the equation for the Green function  $G$  in the form

$$i \frac{dG}{dt} = \delta(t-t') \langle [A(t), B(t')] + \ll [A(t)H(t) - H(t)A(t)]; B(t') \gg \rangle. \quad (2.17)$$

The double-time Green functions on the right hand side of (2.17) are, generally speaking, of higher order than the initial one. We can construct for them also equations of the kind (2.17) and we can obtain a chain of coupled equations for the Green functions. In Secs. 6 to 7 we shall consider actual examples of such chains.

The chains (2.17) are simply the equations of motion for Green functions. They must be supplemented by boundary conditions; this will be done in the following by means of spectral theorems.

We note that we can also obtain other chains for Green functions, for instance, of the Schwinger type,<sup>6</sup> for which multiple-time Green functions must be used. These chains contain quantities in the nature of vertex parts, which depend on three time arguments and for which there are as yet no spectral theorems. In the present survey we shall only use chains of equations similar to (2.17), in which we do not go beyond the limit of the double-time Green functions, and for which there are spectral theorems that facilitate the formulation of boundary conditions.

Equations (2.17) are exact and the solution of this chain of equations is thus extremely complicated in the general statement of the problem. One can sometimes by some approximate method uncouple the chain of Eqs. (2.17), i.e., reduce it to a finite set of equations, which can then be solved. At the present time there are no general prescriptions for such an uncoupling. Only in some limiting cases of model Hamiltonians has it turned out to be possible to perform on the chain of equations an "uncoupling" which is asymptotically exact as  $V \rightarrow \infty$  (see Sec. 6).

### 2.3 Time Correlation Functions

The average over the statistical ensemble of the product of operators in the Heisenberg representation, of the kind

$$\mathcal{F}_{BA}(t, t') = \langle B(t') A(t) \rangle; \quad \mathcal{F}_{AB}(t, t') = \langle A(t) B(t') \rangle \quad (2.18)$$

[the averaging is over the grand canonical ensemble (2.2)], are of importance in statistical mechanics; we shall call these time correlation functions. Indeed, when the times are different ( $t \neq t'$ ) these averages

yield the time correlation functions which are essential for transport processes (see Sec. 4). In the case of statistical equilibrium the functions  $\mathcal{F}_{BA}$  and  $\mathcal{F}_{AB}$  depend, as do the Green functions, only on  $t-t'$  [see (2.9)]

$$\mathcal{F}_{BA}(t, t') = \mathcal{F}_{BA}(t-t'); \quad \mathcal{F}_{AB}(t, t') = \mathcal{F}_{AB}(t-t'). \quad (2.19)$$

In contradistinction to the Green functions (2.8), the time correlation functions do not contain the discontinuous factor  $\theta(t-t')$ , and are defined also when the times are the same,  $t = t'$ . They give then the average values of products of operators

$$\left. \begin{aligned} \mathcal{F}_{BA}(0) &= \langle B(t) A(t) \rangle = \langle B(0) A(0) \rangle, \\ \mathcal{F}_{AB}(0) &= \langle A(t) B(t) \rangle = \langle A(0) B(0) \rangle, \end{aligned} \right\} \quad (2.20)$$

i. e., the usual correlation functions or the distribution functions of statistical mechanics, which enable us to evaluate the average values of dynamical quantities.

For a system of interacting fermions (or bosons) the Hamiltonian has, for instance, in the case of two-body forces, the form

$$H = \sum_p \frac{p^2}{2m} a_p^* a_p + \frac{1}{2V} \sum_{p_1, p_2, p'_1, p'_2} \mathcal{V}(p_1 p_2; p'_1 p'_2) a_{p_1}^* a_{p_2}^* a_{p'_1} a_{p'_2}, \quad (2.21)$$

$$(p_1 + p_2 = p'_1 + p'_2),$$

where  $a_p$  and  $a_p^*$  are fermion (or boson) operators,  $p^2/2m$  is the kinetic energy of the particles, and  $\mathcal{V}(p_1 p_2; p'_1 p'_2)$  are the matrix elements of the interaction energy. We find the average value of the energy by averaging (2.21) over the statistical ensemble (2.2)

$$\langle H \rangle = \sum_p \frac{p^2}{2m} \langle a_p^* a_p \rangle + \frac{1}{2V} \sum_{p_1, p_2, p'_1, p'_2} \mathcal{V}(p_1 p_2; p'_1 p'_2) \langle a_{p_1}^* a_{p_2}^* a_{p'_1} a_{p'_2} \rangle. \quad (2.22)$$

$$(p_1 + p_2 = p'_1 + p'_2).$$

The average energy is in this way expressed in terms of  $\mathcal{F}_{pp}$  and  $\mathcal{F}_{p_1 p_2; p'_1 p'_2}$ , the one-particle and two-particle distribution functions

$$\left. \begin{aligned} \mathcal{F}_{pp} &= \langle a_p^* a_p \rangle, \\ \mathcal{F}_{p_1 p_2; p'_1 p'_2} &= \langle a_{p_1}^* a_{p_2}^* a_{p'_1} a_{p'_2} \rangle, \end{aligned} \right\} \quad (2.23)$$

which are well known in statistical physics (see, for instance, references 21 and 22). The function  $\mathcal{F}_{pp}$  gives the true momentum distribution of the particles, and  $\mathcal{F}_{p_1 p_2; p'_1 p'_2}$  describes the correlation between two particles. Knowledge of the one-particle distribution function enables us to evaluate in general the average values of additive dynamic quantities, the pair distribution function those of binary character, and so on.

The time correlation functions (2.18) satisfy the equations

$$\left. \begin{aligned} i \frac{d}{dt} \mathcal{F}_{BA} &= \langle B(t') \{ A(t) H(t) - H(t) A(t) \} \rangle, \\ i \frac{d}{dt} \mathcal{F}_{AB} &= \langle \{ A(t) H(t) - H(t) A(t) \} B(t') \rangle, \end{aligned} \right\} \quad (2.24)$$

which are obtained by differentiating (2.18) with respect to  $t$  with allowance for the equations of motion for the operators. We note that since (2.18) is not dis-

continuous at  $t = t'$ , Eqs. (2.24) do not have the singular term  $\delta(t - t')$  which occurs in Eqs. (2.17) for the Green functions. The other terms in (2.17) and (2.24) are constructed in the same way, but with the statistical averaging process  $\langle \dots \rangle$  replaced by the  $\langle \dots \rangle_{c, r, a}$  processes [see (2.1)].

The correlation functions can be evaluated either by the direct integration of Eqs. (2.24), to which must be added still the boundary conditions, or indirectly by evaluating first from Eqs. (2.17) the Green functions  $\langle \dots \rangle_{r, a}$  (or  $\langle \dots \rangle_c$ ). The second method which we shall use is considerably simpler, since it makes it easier to satisfy the boundary conditions using spectral theorems (see Sec. 3).

### 3. SPECTRAL REPRESENTATIONS

To solve the equations for the Green functions it is important to have spectral representations that supplement the set of equations with the necessary boundary conditions. In the present section we obtain these relations for the Green functions (2.1a, b, and c) and for the corresponding correlation functions (2.18).

#### 3.1 Spectral Representations for the Time Correlation Functions<sup>10</sup>

We obtain first the spectral representations for the time correlation functions

$$\mathcal{F}_{BA}(t - t') = \langle B(t') A(t) \rangle, \quad \mathcal{F}_{AB}(t - t') = \langle A(t) B(t') \rangle. \quad (3.1)$$

Let  $C_\nu$  and  $E_\nu$  be the eigenfunctions and eigenvalues of the Hamiltonian  $\mathcal{H}$  ( $\mathcal{H} = H - \mu N$ )

$$\mathcal{H}C_\nu = E_\nu C_\nu. \quad (3.2)$$

We write out explicitly the statistical averaging operation in the definition of the time correlation functions (3.1)

$$\langle B(t') A(t) \rangle = Q^{-1} \sum_{\nu, \mu} (C_\nu^* B(t') A(t) C_\nu) e^{-\frac{E_\nu}{\theta}}. \quad (3.3)$$

We use the usual procedure of dispersion relation theory, which is based upon the completeness of the set of functions  $C_\nu$ , and we write Eq. (3.3) in the form

$$\begin{aligned} \langle B(t') A(t) \rangle &= Q^{-1} \sum_{\nu, \mu} (C_\nu^* B(t') C_\mu) (C_\mu^* A(t) C_\nu) e^{-\frac{E_\nu}{\theta}} \\ &= Q^{-1} \sum_{\nu, \mu} (C_\nu^* B(0) C_\mu) (C_\mu^* A(0) C_\nu) e^{-\frac{E_\nu}{\theta}} e^{-i(E_\nu - E_\mu)(t - t')}, \end{aligned} \quad (3.4)$$

since

$$e^{-i\mathcal{H}t} C_\nu = e^{-iE_\nu t} C_\nu, \quad C_\mu^* e^{i\mathcal{H}t} = C_\mu^* e^{iE_\mu t}. \quad (3.5)$$

On the other hand

$$\begin{aligned} \langle A(t) B(t') \rangle &= Q^{-1} \sum_{\nu, \mu} (C_\nu^* A(0) C_\mu) \\ &\times (C_\mu^* B(0) C_\nu) e^{-\frac{E_\nu}{\theta}} e^{-i(E_\nu - E_\mu)(t' - t)}, \end{aligned} \quad (3.6)$$

Interchanging in the last equation the summation indices  $\mu$  and  $\nu$  and comparing (3.4) and (3.6) we note that we can write them in the form<sup>10</sup>

$$\mathcal{F}_{BA}(t - t') = \langle B(t') A(t) \rangle = \int_{-\infty}^{\infty} J(\omega) e^{-i\omega(t - t')} d\omega, \quad (3.7a)$$

$$\mathcal{F}_{AB}(t - t') = \langle A(t) B(t') \rangle = \int_{-\infty}^{\infty} J(\omega) e^{\frac{\omega}{\theta}} e^{-i\omega(t - t')} d\omega, \quad (3.7b)$$

where we have introduced the notation

$$J(\omega) = Q^{-1} \sum_{\nu, \mu} (C_\nu^* A(0) C_\mu) (C_\mu^* B(0) C_\nu) e^{-\frac{E_\mu}{\theta}} \delta(E_\mu - E_\nu - \omega). \quad (3.8)$$

Equations (3.7) are the required spectral representations for the time correlation functions, where  $J(\omega)$  is the spectral intensity of the function  $\mathcal{F}_{BA}(t)$ .

Equations (3.7) can be obtained without using the eigenfunctions of the operator  $\mathcal{H}$ . It is sufficient to note that  $F(t - t')$  depends solely on the difference  $t - t'$ , since the operators under the Sp sign commute; (3.8) is thus simply the definition of the Fourier component. Equation (3.7b) can be obtained from (3.7a) by the substitution  $t - t' \rightarrow t - t' + i/\theta$ , since

$$\langle B(0) A\left(t + \frac{i}{\theta}\right) \rangle = \langle A(t) B(0) \rangle, \quad (3.9)$$

as is easily checked by direct examination.

#### 3.2 Spectral Representations for Retarded and Advanced Green Functions<sup>10, 19</sup>

We consider now the spectral representations for the retarded and advanced Green functions  $G_r(t)$  and  $G_a(t)$  (2.1b and c). We can obtain them easily by means of the spectral representations (3.7a and b) for the time correlation functions. Indeed, let  $G_r(E)$  be the Fourier component of the Green function  $G_r(t - t')$

$$G_r(t - t') = \int_{-\infty}^{\infty} G_r(E) e^{-iE(t - t')} dE, \quad (3.10a)$$

$$G_r(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G_r(t) e^{iEt} dt. \quad (3.10b)$$

(We use the same notation for the Fourier components of the Green functions as for the Green functions themselves.) Substituting into (3.10b) expression (2.8b) for  $G_r(t)$  we get

$$G_r(E) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} dt e^{iE(t - t')} \theta(t - t') \{ \langle A(t) B(t') \rangle - \eta \langle B(t') A(t) \rangle \}. \quad (3.11)$$

Under the integral sign we have here the time correlation functions (3.1). Using for them the spectral representation (3.7a, b), we have

$$\begin{aligned} G_r(E) &= \int_{-\infty}^{\infty} d\omega J(\omega) (e^{\frac{\omega}{\theta}} - \eta) \frac{1}{2\pi i} \int_{-\infty}^{\infty} dt e^{i(E - \omega)t} \theta(t), \\ &(\eta = \pm 1). \end{aligned} \quad (3.12)$$

We can write the discontinuous function  $\theta(t)$  in the form

$$\theta(t) = \int_{-\infty}^t e^{\epsilon t} \delta(t) dt \quad \epsilon \rightarrow 0 \quad (\epsilon > 0) \quad (3.13)$$

or, since

$$\delta(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-ixt} dx, \quad (3.14)$$

in integral form

$$\theta(t) = \frac{i}{2\pi} \int_{-\infty}^{\infty} \frac{e^{-ixt}}{x+i\epsilon} dx. \quad (3.15)$$

One verifies easily that the function defined in this way has, indeed, the properties of the discontinuous  $\theta$  function. We shall consider  $x$  as a complex variable and assume that the integral (3.15) is taken over the contour depicted in Fig. 1. The integrand has a pole in the lower half-plane at  $x = -i\epsilon$ . When  $t > 0$  the contour must be closed in the lower half-plane and the integral (3.15) is equal to unity. When  $t < 0$  the contour must be closed in the upper half-plane and the integral (3.15) vanishes.

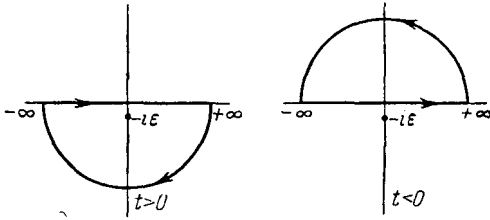


FIG. 1

Using (3.15) and (3.14) we get

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i(E-\omega)t} \theta(t) = \frac{i}{2\pi} \frac{1}{E-\omega+i\epsilon}. \quad (3.16)$$

The Fourier component  $G_r(E)$  of the Green function  $G_r(t)$  is thus equal to

$$G_r(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} (e^{i\theta} - \eta) J(\omega) \frac{d\omega}{E-\omega+i\epsilon}. \quad (3.17)$$

Repeating the same calculation for the Fourier component  $G_a(E)$  of the Green function  $G_a(t)$  we get

$$G_a(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} (e^{i\theta} - \eta) J(\omega) \frac{d\omega}{E-\omega-i\epsilon}. \quad (3.18)$$

Equations (3.17) and (3.18) can be written as one equation

$$G_{r,a}(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} (e^{i\theta} - \eta) J(\omega) \frac{d\omega}{E-\omega \pm i\epsilon} \quad (3.19)$$

(the index  $r$  corresponds to the  $+$  sign and the index  $a$  to the  $-$  sign).

Up to now we have considered  $E$  to be a real quantity. The function (3.19) can be continued analytically in the complex  $E$  plane. Indeed, assuming  $E$  to be complex, we have<sup>19</sup>

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} (e^{i\theta} - \eta) J(\omega) \frac{d\omega}{E-\omega} = \begin{cases} G_r(E) & \text{Im } E > 0 \\ G_a(E) & \text{Im } E < 0. \end{cases} \quad (3.20)$$

The function  $G_{r,a}$  can thus be considered to be one analytical function in the complex plane with a singularity on the real axis. In the following we shall omit

the indices  $r$  and  $a$  and simply write  $G(E)$ , assuming  $E$  to be complex.

The analyticity of  $G(E)$  follows from a theorem proved by N. N. Bogolyubov and O. S. Parasyuk in the theory of dispersion relations.<sup>23</sup> We consider first the analytical properties of the function  $G_r(E)$ ; from (3.10b) we have

$$G_r(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G_r(t) e^{iEt} dt, \quad (3.21)$$

where

$$G_r(t) = 0 \text{ when } t < 0. \quad (3.22)$$

Let us show that the function  $G_r(E)$  can be analytically continued into the region of complex  $E$ . Let  $E$  have a non-vanishing imaginary part

$$E = \text{Re } E + i \text{Im } E = \alpha + i\gamma, \quad \gamma > 0.$$

We then have

$$G_r(\alpha + i\gamma) = \int_0^{\infty} G_r(t) e^{i\alpha t} e^{-\gamma t} dt, \quad \gamma > 0. \quad (3.23)$$

$\text{Exp}(-\gamma t)$  plays the role of a cut-off factor which makes the integral (3.21) and its derivatives with respect to  $E$  convergent under sufficiently general assumptions about the function  $G_r(t)$ .<sup>\*</sup> The function  $G_r(E)$  can thus be analytically continued in the upper half-plane. One can similarly prove that the function  $G_a(E)$  can be analytically continued into the lower half-plane

$$E = \alpha + i\gamma, \quad \gamma < 0.$$

If a cut is made along the real axis, the function

$$G(E) = \begin{cases} G_r(E) & \text{Im } E > 0 \\ G_a(E) & \text{Im } E < 0 \end{cases} \quad (3.24)$$

can be considered to be one analytical function consisting of two branches, one defined in the upper, and the other in the lower half-plane of complex values of  $E$ .

If we know the function  $G(E)$ , we can find also the spectral intensity  $J(\omega)$  of (3.7a) from the relation

$$G(\omega + i\epsilon) - G(\omega - i\epsilon) = -i(e^{i\theta} - \eta) J(\omega) \quad (3.25)$$

( $\omega$  real). Indeed, taking the difference of the two expressions (3.20)

$$\begin{aligned} & G(\omega + i\epsilon) - G(\omega - i\epsilon) \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} (e^{i\theta} - \eta) J(E) \left\{ \frac{1}{\omega - E + i\epsilon} - \frac{1}{\omega - E - i\epsilon} \right\} dE \end{aligned} \quad (3.26)$$

and using the  $\delta$ -function representation

$$\delta(x) = \frac{1}{2\pi i} \left\{ \frac{1}{x - i\epsilon} - \frac{1}{x + i\epsilon} \right\}, \quad (3.27)$$

we arrive at (3.25).

<sup>\*</sup>In order that the Bogolyubov-Parasyuk theorem be valid it is necessary that  $G_r(t)$  be a generalized function in the Sobolev-Schwartz sense.<sup>23</sup>

Were we to decouple in some way the chain of equations (2.17) for the Green functions and to find the Green function  $G(E)$ , we could construct from  $G(E)$  the spectral intensity  $J(\omega)$  of (3.7a) and find expressions for the time correlation functions (3.7a and b).

For instance,

$$\begin{aligned} \mathcal{F}_{BA}(t-t') &= \langle B(t') A(t) \rangle \\ &= i \int_{-\infty}^{\infty} \frac{G(\omega+i\epsilon) - G(\omega-i\epsilon)}{e^{\frac{\omega}{\theta}} - \eta} e^{-i\omega(t-t')} d\omega. \end{aligned} \quad (3.28)$$

In the following we shall show by actual examples how one can sometimes succeed in accomplishing this program.

We give a few other simple relations for Green functions. Using in Eqs. (3.17) and (3.18) the symbolic identity

$$\frac{1}{E-\omega \pm i\epsilon} = P \frac{1}{E-\omega} \mp i\pi\delta(E-\omega), \quad (3.29)$$

where  $\epsilon \rightarrow 0$ ,  $\epsilon > 0$ , and  $P$  denotes the principal value of the integral. We consider here  $E - \omega$  as a real quantity. We find then\*

$$\left. \begin{aligned} G_r(E) &= \frac{1}{2\pi} P \int_{-\infty}^{\infty} (e^{\frac{\omega}{\theta}} - \eta) J(\omega) \frac{d\omega}{E-\omega} - \frac{i}{2} (e^{\frac{E}{\theta}} - \eta) J(E), \\ G_a(E) &= \frac{1}{2\pi} P \int_{-\infty}^{\infty} (e^{\frac{\omega}{\theta}} - \eta) J(\omega) \frac{d\omega}{E-\omega} + \frac{i}{2} (e^{\frac{E}{\theta}} - \eta) J(E), \end{aligned} \right\} (3.30)$$

whence follows a connection between the real and imaginary parts of the Green functions

$$\left. \begin{aligned} \operatorname{Re} G_r(E) &= \frac{P}{\pi} \int_{-\infty}^{\infty} \frac{\operatorname{Im} G_r(\omega)}{\omega-E} d\omega, \\ \operatorname{Re} G_a(E) &= -\frac{P}{\pi} \int_{-\infty}^{\infty} \frac{\operatorname{Im} G_r(\omega)}{\omega-E} d\omega. \end{aligned} \right\} (3.31)$$

Equations (3.31) have the form of dispersion relations. For similar relations for  $G_c$  see the following subsection.

### 3.3 Spectral Representations for Causal Green Functions<sup>12</sup>

The properties of the retarded and advanced Green functions established in the preceding subsection are sufficient for the applications which we shall discuss in the second part of this survey. For the sake of completeness we consider in the present subsection spectral representations for causal Green functions.<sup>12</sup>

We consider the Fourier component  $G_c(E)$  of the causal Green function

$$G_c(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G_c(t) e^{iEt} dt \quad (3.32)$$

( $E$  real). Using (2.8a), (3.7a and b), and (3.15) and integrating, we can write Eq. (3.32) in the form

$$G_c(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} J(\omega) \left\{ \frac{e^{\frac{\omega}{\theta}}}{E-\omega+i\epsilon} - \frac{\eta}{E-\omega-i\epsilon} \right\} d\omega \quad (3.33)$$

or, applying the symbolic identity (3.29) in the form,<sup>12</sup>

$$\begin{aligned} G_c(E) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} (e^{\frac{\omega}{\theta}} - \eta) J(\omega) \\ &\times \left\{ P \frac{1}{E-\omega} - i\pi \frac{e^{\frac{\omega}{\theta}} + \eta}{e^{\frac{\omega}{\theta}} - \eta} \delta(E-\omega) \right\} d\omega. \end{aligned} \quad (3.34)$$

Separating the real and imaginary parts of (3.34) we get

$$\left. \begin{aligned} \operatorname{Re} G_c(E) &= \frac{1}{2\pi} P \int_{-\infty}^{\infty} (e^{\frac{\omega}{\theta}} - \eta) J(\omega) \frac{d\omega}{E-\omega}, \\ \operatorname{Im} G_c(E) &= -\frac{1}{2} (e^{\frac{E}{\theta}} + \eta) J(E), \end{aligned} \right\} (3.35)$$

whence follows a relation between the real and imaginary parts of the Green function  $G_c(E)$ , first obtained for the single-particle Green function by L. D. Landau<sup>12</sup>

$$\operatorname{Re} G_c(E) = \frac{P}{\pi} \int_{-\infty}^{\infty} \frac{e^{\frac{\omega}{\theta}} - \eta}{e^{\frac{\omega}{\theta}} + \eta} \frac{\operatorname{Im} G_c(\omega)}{\omega-E} d\omega. \quad (3.36)$$

[Equation (3.36) was applied to the theory of superconductivity in reference 16.]  $E$  is real in Eqs. (3.32) to (3.36). We shall not use the causal Green functions for they cannot be analytically continued into the complex  $E$  plane, and are thus inconvenient to apply.

## 4. GREEN FUNCTIONS IN THE THEORY OF IRREVERSIBLE PROCESSES<sup>10</sup>

Green functions are not only applied to the case of statistical equilibrium. They are a convenient means of studying processes where the deviation from the state of statistical equilibrium is small. It then turns out to be possible to evaluate the transport coefficients of these processes in terms of Green functions evaluated for the unperturbed equilibrium state without explicitly having recourse to setting up a transport equation.

### 4.1 The Reaction of a System to an External Perturbation

We consider the reaction of a quantum-mechanical system with a time-independent Hamiltonian  $H$  when an external perturbation  $H_t$  is switched on. The total Hamiltonian is equal to

\*Equation (3.30) expresses the well-known properties of the limiting values of a Cauchy type integral which was first established by Yu. V. Sokhotskiĭ in 1873 and later by K. Plemel in 1908 [see M. A. Lavrent'ev and B. V. Shabat, *Методы теории функций комплексного переменного*, (Methods of the theory of functions of a complex variable), Gostekhizdat, Moscow, 1958].

$$H + H_i^1, \quad (4.1)$$

where we assume that there is no external perturbation at  $t = -\infty$

$$H_i^1|_{t=-\infty} = 0.$$

In the case of an adiabatic switching on of a periodic perturbation we have, for instance,

$$H_i^1 = \sum_{\Omega} e^{\epsilon t} e^{-i\Omega t} V_{\Omega} \quad (\epsilon \rightarrow 0 \quad \epsilon > 0) \quad (4.2)$$

or in the case of an instantaneous switching on of a perturbation

$$H_i^1 = \begin{cases} 0, & t < t_0, \\ \sum_{\Omega} e^{-i\Omega t} V_{\Omega}, & t > t_0, \end{cases} \quad (4.3)$$

where  $V_{\Omega}$  is an operator which does not explicitly depend on the time. Let  $A$  be a dynamical variable which does not explicitly depend on the time either. We consider the influence of the switching on of the perturbation (4.2) or (4.3) on the average value of the operator  $A$ .

The average value of  $A$  is

$$\bar{A}(t) = \text{Sp} \{ \rho(t) A \}, \quad (4.4)$$

where  $\rho(t)$  is a statistical operator which satisfies the equation of motion

$$i \frac{d\rho(t)}{dt} = [H + H_i^1, \rho(t)] \quad (4.5)$$

and the initial condition

$$\rho(t)|_{t=-\infty} = \rho = Q^{-1} e^{-\frac{H}{\theta}} \quad (Q = \text{Sp} e^{-\frac{H}{\theta}}), \quad (4.5')$$

which means that the system was at  $t = -\infty$  in a state of statistical equilibrium.

We look for a solution of Eq. (4.5) of the form

$$\rho(t) = \rho + \Delta\rho. \quad (4.6)$$

Neglecting terms  $H_i^1 \Delta\rho$ , since we have assumed that the system is only little removed from a state of statistical equilibrium, we get then

$$i \frac{d}{dt} \Delta\rho = [H, \Delta\rho] + [H_i^1, \rho], \quad (4.7)$$

where

$$\Delta\rho(t)|_{t=-\infty} = 0.$$

Processes for which we can restrict ourselves in Eq. (4.4) to terms linear in the perturbation are called linear dissipative processes. (For a discussion of higher-order terms see reference 10.)

To solve Eq. (4.7) we introduce the operator

$$\Delta\rho_1 = e^{iHt} \Delta\rho e^{-iHt} \quad (4.8)$$

and, taking into account that  $\rho$  and  $H$  commute, we find

$$i \frac{d}{dt} \Delta\rho_1 = e^{iHt} [H_i^1, \rho] e^{-iHt}, \quad (4.9)$$

$$\Delta\rho_1(-\infty) = 0.$$

From this we find after integration

$$\Delta\rho(t) = \frac{1}{i} \int_{-\infty}^t e^{iH(t-\tau)} [H_{\tau}^1, \rho] e^{-iH(t-\tau)} d\tau. \quad (4.10)$$

Substituting (4.6) and (4.10) into (4.4) we get

$$\bar{A}(t) = \langle A \rangle + \frac{1}{i} \int_{-\infty}^t \langle [A(t), H_{\tau}^1(\tau)] \rangle d\tau, \quad (4.11)$$

where

$$A(t) = e^{iHt} A e^{-iHt}, \quad H_i^1(t) = e^{iHt} H_i^1 e^{-iHt} \quad (4.12)$$

is the Heisenberg representation for the operators  $A$  and  $H_i^1$ .

Taking (4.2) into account we can write (4.11) in the form\*

$$\bar{A}(t) = \langle A \rangle + \sum_{\Omega} \frac{1}{i} \int_{-\infty}^t \langle [A(t), V_{\Omega}(\tau)] \rangle e^{-i\Omega\tau + \epsilon\tau} d\tau. \quad (4.13)$$

Introducing under the integral sign the function  $\theta(t - \tau)$  and extending the limit of integration to  $\tau = \infty$  we use the definitions (2.1b) and (3.10b) to rewrite (4.13) in the form

$$\bar{A}(t) = \langle A \rangle + \sum_{\Omega} e^{-i\Omega t + \epsilon t} 2\pi \langle \langle A | V_{\Omega} \rangle \rangle_{E=\Omega}^{\text{ret}}, \quad (4.14)$$

where  $\langle \langle A | V_{\Omega} \rangle \rangle_{E=\Omega}^{\text{ret}}$  is the Fourier component (for  $E=\Omega$ ) of the retarded Green function  $\langle \langle A(t); V_{\Omega}(\tau) \rangle \rangle_{\tau}$ , ( $\eta = -1$ ).

The change in the average value of an operator when a periodic perturbation is switched on adiabatically can thus be expressed in terms of the Fourier components of the retarded Green functions which connect the perturbation operator and the observed quantity.

In the case of an instantaneous switching on of the interaction we substitute (4.3) into (4.11) and get

$$\bar{A}(t) = \langle A \rangle + \sum_{\Omega} \int_{t_0}^{\infty} \langle \langle A(t); V_{\Omega}(\tau) \rangle \rangle_{\tau}^{\text{ret}} e^{-i\Omega\tau + \epsilon\tau} d\tau, \quad (4.15)$$

i.e., the reaction of the system can also be expressed in terms of the retarded Green functions. Equations (4.13) and (4.14) are well known in the statistical mechanics of irreversible processes, where the retarded Green functions are usually called the after-effect functions.

The particular case where the external perturbation is periodic in time and contains only one harmonic frequency  $\omega$  is of interest. Putting in that case  $\Omega = \pm \omega$  in (4.2), since

$$H_i^1 = -\mathcal{F}_0 \cos \omega t e^{\epsilon t} B, \quad (4.16)$$

where  $\mathcal{F}_0$ , the amplitude of the periodic force, is a c number and where  $B$  is the operator part of the per-

\*Here and henceforth in this section, unlike in (2.1), the averaging is over a canonical ensemble, and the operators are in the Heisenberg representation with the Hamiltonian  $H$  and not with  $\mathcal{H} = H - \mu N$ .



turbation, we get from Eq. (4.14)

$$\bar{A}(t) = \langle A \rangle - \mathcal{F}_0 e^{-i\omega t + \varepsilon t} \pi \langle \langle A | B \rangle \rangle_{E=\omega}^{\text{ret}} - \mathcal{F}_0 e^{i\omega t + \varepsilon t} \pi \langle \langle A | B \rangle \rangle_{E=-\omega}^{\text{ret}} \quad (4.17)$$

or, taking into account that  $\bar{A}(t)$  is a real quantity

$$\bar{A}(t) = \langle A \rangle + \text{Re} \{ \chi(\omega) \mathcal{F}_0 e^{-i\omega t + \varepsilon t} \}, \quad (4.18)$$

where  $\text{Re}$  indicates the real part of the expression and  $\chi(\omega)$  is the complex admittance, equal to

$$\chi(\omega) = -2\pi \langle \langle A | B \rangle \rangle_{E=\omega}^{\text{ret}}. \quad (4.19)$$

Equations (4.18) and (4.19) elucidate the physical meaning of the Fourier components of the Green function  $\langle \langle A(t)B(\tau) \rangle \rangle^{\text{ret}}$  as being the complex admittance that describes the influence of the periodic perturbation (4.16) on the average value of the quantity  $A$ .

## 4.2 The Electrical Conductivity Tensor

As an example we consider the connection between the electrical conductivity tensor and Green functions<sup>10</sup>. Let there be switched on adiabatically an electrical field  $E(t)$ , uniform in space and changing periodically in time with a frequency  $\omega$

$$E(t) = E \cos \omega t.$$

The corresponding perturbation operator is equal to

$$H_1^i = - \sum_j e_j (E x_j) \cos \omega t e^{\varepsilon t} \quad (4.20)$$

(where  $e_j$  is the charge of the  $j$ -th particle, and where the summation is over all particle coordinates  $\mathbf{x}_j$ ). Under the influence of the perturbation (4.20) there arises in the system an electrical current

$$j_\alpha(t) = \int_{-\infty}^{\infty} \langle \langle j_\alpha(t); H_1^i(\tau) \rangle \rangle d\tau, \quad (4.21)$$

where

$$\begin{aligned} H_1^i(\tau) &= H^1(\tau) \cos \omega \tau e^{\varepsilon \tau}, \\ H^1(t) &= - \sum_{j,\alpha} e_j E_\alpha x_{\alpha j}(\tau), \\ j_\alpha(t) &= \sum_j e_j \dot{x}_{\alpha j}(t), \end{aligned} \quad (4.22)$$

$j_\alpha$  is the current density operator, if the volume of the system is taken to be unity. Integrating by parts, we write Eq. (4.21) in the form

$$\begin{aligned} j_\alpha(t) &= - \text{Re} \left\{ \int_{-\infty}^{\infty} \langle \langle j_\alpha(t); H^1(\tau) \rangle \rangle \frac{e^{i\omega t + \varepsilon \tau} d\tau}{i\omega + \varepsilon} \right. \\ &\quad \left. + \langle \langle j_\alpha(0); H^1(0) \rangle \rangle e^{i\omega t + \varepsilon t} \frac{1}{\omega - i\varepsilon} \right\}. \end{aligned} \quad (4.23)$$

Noting that

$$\dot{H}^1(\tau) = -(E \mathbf{j}(\tau)), \quad [\dot{x}_{\alpha j_1}, x_{\beta j_2}] = -\frac{i}{m} \delta_{\alpha\beta} \delta_{j_1 j_2} \quad (\hbar = 1),$$

we get from this equation

$$j_\alpha(t) = \text{Re} \{ \sigma_{\alpha\beta}(\omega) E_\beta e^{i\omega t + \varepsilon t} \}, \quad (4.24)$$

$$\sigma_{\alpha\beta}(\omega) = -\frac{ie^{2n}}{m\omega} \delta_{\alpha\beta} + \int_{-\infty}^{\infty} \langle \langle j_\alpha(0); j_\beta(\tau) \rangle \rangle \frac{e^{i\omega\tau + \varepsilon\tau}}{i\omega + \varepsilon} d\tau \quad (4.25)$$

is the electrical conductivity tensor, and  $n$  the number of electrons per unit volume. The first term in (4.25) corresponds to the electrical conductivity of a system of free charges and is not connected with the interparticle interaction. As  $\omega \rightarrow \infty$  the second term decreases more strongly than the first one  $\lim_{\omega \rightarrow \infty} \text{Im} \omega \sigma_{\alpha\beta}(\omega) = -e^{2n} \delta_{\alpha\beta} / m$ , and the system behaves as a collection of free charges.

One can use (3.7) and integrate over  $\tau$  to rewrite Eq. (4.25) in a different, equivalent form

$$\sigma_{\alpha\beta}(\omega) = -\frac{ie^{2n}}{m\omega} \delta_{\alpha\beta} + \frac{e^{-\frac{\omega}{\theta}} - 1}{\omega} \int_{-\infty}^{\infty} \langle \langle j_\alpha(0) j_\beta(t) \rangle \rangle e^{-i\omega t} dt. \quad (4.26)$$

This is Nyquist's well-known theorem,<sup>24</sup> generalized by Callen and Welton<sup>9</sup> for the quantum mechanical case; it connects the electrical conductivity with the fluctuating currents. It is usually written in a somewhat different form<sup>10</sup>

$$\sigma_{\alpha\beta}(\omega) = -\frac{ie^{2n}}{m\omega} \delta_{\alpha\beta} + \frac{1}{\omega} \text{th} \frac{\omega}{2\theta} \int_{-\infty}^{\infty} \langle \langle j_\alpha(0) j_\beta(t) \rangle \rangle e^{-i\omega t} dt, \quad (4.27)$$

where

$$\langle \langle A(t) B(t') \rangle \rangle = \frac{1}{2} \langle \langle A(t) B(t') + B(t') A(t) \rangle \rangle$$

are the symmetrized time correlation functions. Using Eq. (4.27) one can evaluate the electrical conductivity without constructing a transport equation.<sup>25</sup>

Equations (4.25) to (4.27) are noteworthy as they connect a characteristic of a non-equilibrium state, the electrical conductivity, with the correlation function of the currents in the state of statistical equilibrium. Kirkwood<sup>26</sup> was the first to obtain such a relation for the coefficient of internal friction. They also occur for other transport coefficients, for instance, diffusion and thermal-diffusion coefficients, the magnetic-susceptibility tensor, and so on. We shall not dwell on these problems, but refer the reader to the literature.<sup>10, 18, 27-29</sup>

For applications of Green functions to the theory of irreversible processes, see especially references 10 and 18 where the fluctuation dissipation theorem and dispersion relations for transport coefficients are considered in more detail.

## 5. PERFECT QUANTUM GASES

As a simple illustration of the method, we consider the Green functions for perfect quantum gases. The Hamiltonian of a perfect gas of fermions (or bosons) is of the form

$$\mathcal{H} = \sum_f T_f a_f^\dagger a_f, \quad (5.1)$$

where  $f = (\mathbf{k}, \sigma)$ ,  $\sigma$  is the spin index,  $\mathbf{k}$  the momentum (for a boson gas  $\sigma = 0$ ),  $T_f = \mathbf{k}^2 / 2m - \mu$ ,  $\mu$  the chemical

potential, while  $a_f$  and  $a_f^\dagger$  are operators satisfying the Fermi-Dirac and Bose-Einstein statistics commutation relations,

$$\left. \begin{aligned} a_f a_f^\dagger - \epsilon a_f^\dagger a_f &= \delta_{ff'}, \\ a_f a_{f'} - \epsilon a_{f'} a_f &= a_f^\dagger a_{f'}^\dagger - \epsilon a_{f'}^\dagger a_f^\dagger = 0 \end{aligned} \right\} \quad (5.2)$$

(for Fermi-Dirac statistics  $\epsilon = -1$ , and for Bose-Einstein statistics  $\epsilon = +1$ ). The quantum mechanical equations of motion (2.14) for the operators are very simple

$$i \frac{da_f}{dt} = T_f a_f; \quad i \frac{da_f^\dagger}{dt} = -T_f a_f^\dagger. \quad (5.3)$$

We introduce the Green function ( $\eta = \epsilon$ )

$$G_f(t-t') = \langle \langle a_f(t); a_f^\dagger(t') \rangle \rangle, \quad (5.4)$$

corresponding to the following choice in Eqs. (2.1b and c)

$$A(t) = a_f(t), \quad B(t') = a_f^\dagger(t'), \quad (5.5)$$

and construct with it the equation of motion (2.15)

$$i \frac{dG_f}{dt} = \delta(t-t') + T_f G_f. \quad (5.6)$$

One can easily solve Eq. (5.6).

Going over to the Fourier components of the Green functions

$$G_f(t-t') = \int_{-\infty}^{\infty} G_f(E) e^{-iE(t-t')} dE$$

and using the  $\delta$ -function representation

$$\delta(t-t') = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-iE(t-t')} dE, \quad (5.7)$$

we get

$$(E - T_f) G_f(E) = \frac{1}{2\pi}. \quad (5.8)$$

The Green function  $G_f(E)$  is thus equal to

$$G_f(E) = \frac{1}{2\pi} \frac{1}{E - T_f}. \quad (5.9)$$

One could still add to the solution (5.9) a singular part of the form  $\delta(E - T_f)$  with an arbitrary coefficient. The function obtained in that way would, however, not satisfy the analytical properties of the retarded (or advanced) Green function (see Sec. 3.2), so that we must set the coefficient of the  $\delta$  function equal to zero; (5.9) gives thus the required solution. For the causal Green functions we must take into account the singular addition to the solution (5.9) in order that the Green functions possess the necessary analytical properties (see Sec. 3.3). It is thus clear from (5.9) that the Green functions have a pole at  $E = T_f$ ; the energy of the elementary excitations  $E(f) = T_f$  corresponds thus to the pole of the Green function. We find the spectral intensity  $J(\omega)$  of the corresponding correlation function

$$\mathcal{F}_f(t-t') = \langle a_f^\dagger(t') a_f(t) \rangle = \int_{-\infty}^{\infty} J_f(\omega) e^{-\omega(t-t')} d\omega \quad (5.10)$$

by using Eq. (3.25)

$$G_f(\omega + i\epsilon) - G_f(\omega - i\epsilon) = -i \left( e^{\frac{\omega}{\theta}} - \eta \right) J_f(\omega)$$

and the  $\delta$ -function representation (3.27), and we have

$$J_f(\omega) = \frac{\delta(\omega - T_f)}{e^{\frac{\omega}{\theta}} - \eta}. \quad (5.11)$$

We see that for perfect gases the spectral intensity  $J(\omega)$  has a  $\delta$ -function shape. We get for  $\mathcal{F}_f(t-t')$

$$\mathcal{F}_f(t-t') = \langle a_f^\dagger(t') a_f(t) \rangle = \frac{e^{-iT_f(t-t')}}{e^{\frac{T_f}{\theta}} - \eta}. \quad (5.12)$$

Putting  $t = t'$  in (5.12) we find the average occupation number

$$\bar{n}_f = \langle a_f^\dagger a_f \rangle = \left\{ e^{\frac{T_f}{\theta}} - \eta \right\}^{-1}. \quad (5.13)$$

We determine the chemical potential  $\mu$  from the condition

$$\sum_f \left\{ e^{\frac{T_f}{\theta}} - \eta \right\}^{-1} = N. \quad (5.14)$$

We note that we need not evaluate the partition function in order to calculate  $\bar{n}_f$ . Instead we solve the equations for the Green function and use the spectral theorem (3.25).

The example given here has a purely illustrative character; one need not apply Green function techniques to consider perfect gases. We only gave this example to show for a very simple case the general pattern of consideration, which is the same for other, no longer trivial examples. One can also evaluate the Green functions of a perfect gas directly, using the definitions (2.1) to (2.5), the commutation relations (5.2) for the operators, and the fact that for a perfect gas

$$\left. \begin{aligned} a_f(t) &= e^{iHt} a_f e^{-iHt} = e^{-iT_f t} a_f, \\ a_f^\dagger(t) &= e^{iHt} a_f^\dagger e^{-iHt} = e^{iT_f t} a_f^\dagger. \end{aligned} \right\} \quad (5.15)$$

We then find for the Green functions

$$\left. \begin{aligned} G_f^c(t-t') &= \langle \langle a_f(t) a_f^\dagger(t') \rangle \rangle_c \\ &= -i\theta(t-t') e^{-iT_f(t-t')} (1 + \eta \bar{n}_f) - i\eta\theta(t'-t) e^{-T_f(t-t')} \bar{n}_f, \\ G_f^r(t-t') &= \langle \langle a_f(t) a_f^\dagger(t') \rangle \rangle_r = -i\theta(t-t') e^{-iT_f(t-t')}, \\ G_f^a(t-t') &= \langle \langle a_f(t) a_f^\dagger(t') \rangle \rangle_a = i\theta(t'-t) e^{-iT_f(t-t')} \end{aligned} \right\} \quad (5.16)$$

and, using (3.15), we get for the corresponding Fourier components

$$\left. \begin{aligned} G_f^c(E) &= \frac{1}{2\pi} \left\{ \frac{1 + \eta \bar{n}_f}{E - T_f + i\epsilon} - \frac{\eta \bar{n}_f}{E - T_f - i\epsilon} \right\}, \\ G_f^r(E) &= \frac{1}{2\pi} \frac{1}{E - T_f + i\epsilon}, \\ G_f^a(E) &= \frac{1}{2\pi} \frac{1}{E - T_f - i\epsilon}. \end{aligned} \right\} \quad (5.17)$$

We note that the retarded and advanced Green functions for a perfect gas are temperature-independent.

In the remainder of the present paper we shall only

deal with retarded and advanced Green functions (2.1b and c) without specifically mentioning this.

## 6. APPLICATION TO THE THEORY OF SUPERCONDUCTIVITY

It has been shown in references 30 to 32 that one can develop a theory of superconductivity starting from the Bardeen-Cooper-Schrieffer model Hamiltonian, in which the electron-phonon interaction is replaced by a direct electron-electron interaction, and in which one takes into account only the interactions of pairs of electrons with opposite momenta and spins. It was shown that this interaction was the basic one responsible for the phenomenon of superconductivity. In reference 31, where the theory of superconductivity was developed starting from Fröhlich's exact Hamiltonian in which the emission and absorption of lattice phonons is taken into account explicitly, the possibility of replacing the Hamiltonian by a model Hamiltonian was in particular put on a firm basis and the choice of its parameters was made more precise. In the present section we consider the application of retarded and advanced Green functions to the theory of superconductivity, based upon a model Hamiltonian of such a type. (Causal Green functions were applied to the theory of superconductivity in references 16, 34, and 35.)

The consideration of the model Hamiltonian is of

$$\left. \begin{aligned} J\left(k, \frac{1}{2}; k', \frac{1}{2}\right) &= J\left(k, -\frac{1}{2}; k', -\frac{1}{2}\right) = \frac{1}{2} J(k, k') > 0, \\ J\left(-k, -\frac{1}{2}; k', \frac{1}{2}\right) &= J\left(k, \frac{1}{2}; -k', -\frac{1}{2}\right) = -\frac{1}{2} J(k, -k'), \\ (J(k, k') &= J(-k, -k')) \end{aligned} \right\} \quad (6.3)$$

or

$$J(f, f') = \frac{1}{2} \{J(k, k') \delta_{\sigma-\sigma'} - J(k, -k') \delta_{\sigma+\sigma'}\}. \quad (6.4)$$

When (6.3) holds, the Hamiltonian (6.1) is of the form

$$\begin{aligned} \mathcal{H} &= \sum_{k, \sigma} \left( \frac{k^2}{2m} - \mu \right) a_{k\sigma}^* a_{k\sigma} \\ &- \frac{1}{V} \sum_{k, k'} J(k, k') a_{k, \frac{1}{2}}^* a_{-k, -\frac{1}{2}}^* a_{-k', -\frac{1}{2}} a_{k', \frac{1}{2}} \end{aligned} \quad (6.5)$$

We note an interesting property of the model Hamiltonian (6.1). If we choose as the zeroth-order Hamiltonian the Hamiltonian  $\mathcal{H}_0$  of non-interacting particles, as is done in the usual perturbation theory, the operator  $H_{\text{int}}$  will give an asymptotically small contribution to the energy of the system and to the other thermodynamic functions as  $V \rightarrow \infty$  in all orders of the statistical perturbation theory. In first order we get, for instance,

$$\langle H_{\text{int}} \rangle = -\frac{1}{V} \sum_f J(f, f) \langle n_f \rangle^2,$$

which is finite as  $V \rightarrow \infty$ . One sees easily that this property is conserved also in higher orders. Since, however, the ratio of  $\langle H \rangle$  to  $V$  must tend to a finite

interest as one can get a solution which is asymptotically exact as  $V \rightarrow \infty$  ( $V/N = \text{const.}$ ) (see references 32, 63, and 65). One need therefore not make any approximations to decouple the chains of equations for the Green functions, for the decoupling turns out to be asymptotically exact. The solution of a model example can, among other things, serve to indicate possible approximations when solving other examples, no longer of the model type.

### 6.1. The Model Hamiltonian

We shall start from a model Hamiltonian of the form

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_0 + H_{\text{int}} = \sum_f T_f a_f^* a_f \\ &- \frac{1}{2V} \sum_{f, f'} J(f, f') a_f^* a_{-f}^* a_{-f'} a_{f'}, \end{aligned} \quad (6.1)$$

where  $f = (k, \sigma)$ ,  $-f = (-k, -\sigma)$ ,  $\sigma$  is the spin index which takes on the two values  $+\frac{1}{2}$  and  $-\frac{1}{2}$ ,  $k$  is the momentum,  $T_f = k^2/2m - \mu$ ,  $\mu$  is the chemical potential,  $a_f$  and  $a_f^*$  are operators satisfying the Fermi-Dirac statistics commutation relations (5.2), and  $J(f, f')$  is a real function with the properties

$$\left. \begin{aligned} J(-f, f') &= -J(f, f'), & J(f, -f') &= -J(f, f'), \\ J(f, f') &= J(f', f). \end{aligned} \right\} \quad (6.2)$$

In the case of Bardeen's model one must put

limit when the limit  $V \rightarrow \infty$  is taken, the operator  $H_{\text{int}}$  gives an asymptotically small contribution in all orders of the usual perturbation theory. It is, on the other hand, well known<sup>30,32</sup> that the model interaction turns out to be important and gives a finite contribution to the thermodynamic functions. The Hamiltonian (6.1) is therefore an example of such an interaction which gives zero (as  $V \rightarrow \infty$ ) in each term of perturbation theory and leads to a finite effect for the whole series. This is apparently connected with the fact that the effect of the terms in the perturbation theory series begins to show up starting with large  $n \sim n_0$ , where  $n_0 \rightarrow \infty$  together with  $N$  ( $N$  is the number of particles). In the usual considerations these terms are assumed to be infinitesimally small and are not taken into account. A similar situation occurs in the usual condensation theory where it is necessary to take into account groups of large numbers of molecules.<sup>33</sup>

### 6.2. The Application of Green Functions

We consider now the application of retarded and advanced Green functions to the Hamiltonian (6.1). We construct first the quantum mechanical equations of motion (2.15) for the operators  $a_f$  and  $a_f^*$

$$\left. \begin{aligned} i \frac{da_j}{dt} &= T_j a_j - \frac{1}{V} \sum_{f'} J(f, f') a_{-f}^{\dagger} a_{-f'} a_{f'} \\ i \frac{da_j^{\dagger}}{dt} &= -T_j a_j^{\dagger} + \frac{1}{V} \sum_{f'} J(f, f') a_j^{\dagger} a_{-f'}^{\dagger} a_{f'} \end{aligned} \right\} \quad (6.6)$$

We introduce the Green function

$$G_f(t-t') = \langle \langle a_j(t); a_j^{\dagger}(t') \rangle \rangle \quad (\eta = -1) \quad (6.7)$$

and write down for it the equation of motion (2.17)

$$\begin{aligned} i \frac{dG_f}{dt} &= \delta(t-t') + T_j G_f \\ &- \frac{1}{V} \sum_{f'} J(f, f') \langle \langle a_{-f}^{\dagger} a_{-f'} a_{f'}; a_j^{\dagger}(t') \rangle \rangle \end{aligned} \quad (6.8)$$

(for the sake of brevity we have omitted the argument  $t$  of the operators). The equation for  $G_f$  contains also the double-time Green function  $\Gamma_{ff}$

$$\Gamma_{ff'}(t-t') = \langle \langle a_{-f}^{\dagger}(t) a_{-f'}(t) a_{f'}; a_j^{\dagger}(t') \rangle \rangle. \quad (6.9)$$

We construct for this function, too, an equation of motion

$$\begin{aligned} i \frac{d\Gamma_{ff'}}{dt} &= \delta(t-t') n_{-f} (\delta_{f-f'} - \delta_{f+f'}) + (2T_{f'} - T_f) \Gamma_{ff'} \\ &- \frac{1}{V} \sum_g J(f, g) \langle \langle a_g^{\dagger} a_{-g}^{\dagger} a_{-f'} a_{f'}; a_j^{\dagger}(t') \rangle \rangle \\ &- \frac{1}{V} \sum_g J(f', g) \langle \langle (1 - n_{-f'} - n_{f'}) a_{-f}^{\dagger} a_{-g} a_g; a_j^{\dagger}(t') \rangle \rangle \\ &- \frac{1}{V} \sum_g J(f', g) \Gamma_{fg} (\delta_{f+f'} + \delta_{f-f'}). \end{aligned} \quad (6.10)$$

The Green function (6.9) corresponds to the following choice in (2.1b and c)

$$A = a_{-f}^{\dagger} a_{-f'} a_{f'}, \quad B = a_j^{\dagger}. \quad (6.11)$$

We note that the quantity  $\Gamma_{ff'}$  occurs in Eq. (6.8) for  $G_f$  in the sum over  $f'$  with a factor  $V^{-1}$ . We can thus neglect with asymptotical exactness in Eq. (6.10) for  $\Gamma_{ff'}$  the terms with  $\delta_{f+f'}$  and  $\delta_{f-f'}$ . For the same reason the average of the product of the operators  $n_{f'}$  and

$$\frac{1}{V} \sum_g J(f', g) a_{-f}^{\dagger} a_{-g} a_g a_j^{\dagger}$$

in the second sum in Eq. (6.10) can be replaced, also asymptotically exactly, by the product of the averages, taking into consideration that the average values of these operators are macroscopic quantities which are finite as  $V \rightarrow \infty$ . We can thus put\*

\*The fact that the solution corresponding to such a decoupling is the same as the Bardeen-Cooper-Schrieffer solution<sup>30</sup> (see next subsection) shows that this decoupling is, indeed, asymptotically exact as  $V \rightarrow \infty$ , since the asymptotic exactness of the latter was proved in reference 32 by perturbation theory and in references 63 and 65 without perturbation theory. In references 63 and 65 it was also shown that one can satisfy the complete chain of equations for the Green functions which are constructed on the basis of the model Hamiltonian.

$$\begin{aligned} &\langle \langle (1 - n_{-f'} - n_{f'}) a_{-f}^{\dagger} a_{-g} a_g; a_j^{\dagger}(t') \rangle \rangle \\ &= (1 - \bar{n}_{-f'} - \bar{n}_{f'}) \langle \langle a_{-f}^{\dagger} a_{-g} a_g; a_j^{\dagger}(t') \rangle \rangle. \end{aligned}$$

Repeating these considerations also for the first sum in Eq. (6.10) we can write Eqs. (6.8) and (6.10) in the form

$$\left. \begin{aligned} i \frac{dG_f}{dt} &= \delta(t-t') + T_j G_f - \frac{1}{V} \sum_{f'} J(f, f') \Gamma_{ff'}, \\ i \frac{d\Gamma_{ff'}}{dt} &= (2T_{f'} - T_f) \Gamma_{ff'} - \\ &- \frac{1}{V} \sum_g J(f, g) \langle a_g^{\dagger} a_{-g}^{\dagger} a_{-f'} a_{f'} \rangle G_f - \\ &- \frac{1}{V} \sum_g J(f', g) (1 - \bar{n}_{-f'} - \bar{n}_{f'}) \Gamma_{fg}. \end{aligned} \right\} \quad (6.12)$$

Changing to the Fourier components (3.10) of the Green functions

$$\left. \begin{aligned} G_f(t-t') &= \int_{-\infty}^{\infty} G_f(E) e^{-iE(t-t')} dE, \\ \Gamma_{ff'}(t-t') &= \int_{-\infty}^{\infty} \Gamma_{ff'}(E) e^{-iE(t-t')} dE \end{aligned} \right\} \quad (6.13)$$

(we use the same notation for the Green functions and for their Fourier components) we can write the set of equations for  $G_f(E)$  and  $\Gamma_{ff'}(E)$  in a form which does no longer contain time derivatives

$$\begin{aligned} EG_f &= \frac{1}{2\pi} + T_j G_f - \frac{1}{V} \sum_{f'} J(f, f') \Gamma_{ff'}, \\ E\Gamma_{ff'} &= (2T_{f'} - T_f) \Gamma_{ff'} - \frac{1}{V} \sum_g J(f, g) \langle a_g^{\dagger} a_{-g}^{\dagger} a_{-f'} a_{f'} \rangle G_f \\ &- \frac{1}{V} \sum_g J(f', g) (1 - \bar{n}_{-f'} - \bar{n}_{f'}) \Gamma_{fg}. \end{aligned} \quad (6.14)$$

We obtain thus a set of integral equations for the functions  $G_f(E)$  and  $\Gamma_{ff'}(E)$ . One notes easily that the solution of Eq. (6.14) can be found in the form

$$\langle a_g^{\dagger} a_{-g}^{\dagger} a_{-f'} a_{f'} \rangle = A_g A_{f'}, \quad \Gamma_{ff'} = \Gamma_f A_{f'} \quad (A_f^{\dagger} = A_f). \quad (6.15)$$

Indeed, we get for  $G_f$  and  $\Gamma_f$  the equations (compare reference 34)

$$\left. \begin{aligned} (E - T_f) G_f - L_f \Gamma_f &= \frac{1}{2\pi}, \\ (E + T_f) \Gamma_f - L_f G_f &= 0, \end{aligned} \right\} \quad (6.16)$$

where we put, moreover,

$$2T_{f'} + \frac{1 - 2\bar{n}_{f'}}{A_{f'}} L_{f'} = 0 \quad (6.17)$$

and introduce the notation

$$L_f = -\frac{1}{V} \sum_g J(f, g) A_g. \quad (6.18)$$

Solving the set (6.16) we get

$$G_f(E) = \frac{1}{2\pi} \frac{E + T_f}{E^2 - T_f^2 - L_f^2}, \quad \Gamma_f(E) = \frac{1}{2\pi} \frac{L_f}{E^2 - T_f^2 - L_f^2}. \quad (6.19)$$

The poles of the Green functions (6.19) give for the

spectrum of elementary excitations the expression<sup>30</sup>

$$\omega_j = \sqrt{T_j^2 + L_j^2}. \quad (6.20)$$

Using (6.20) one can conveniently write the Green functions in the form

$$G_j(E) = \frac{1}{4\pi} \left\{ \left(1 + \frac{T_j}{\omega_j}\right) \frac{1}{E - \omega_j} + \left(1 - \frac{T_j}{\omega_j}\right) \frac{1}{E + \omega_j} \right\},$$

$$\Gamma_{j'j''}(E) = \frac{1}{4\pi\omega_j} A_{j'} L_j \left\{ \frac{1}{E - \omega_j} - \frac{1}{E + \omega_j} \right\}. \quad (6.21)$$

One can easily evaluate the spectral intensities of the time correlation functions  $I_f(\omega)$

$$\langle a_j^\dagger(t') a_j(t) \rangle = \int_{-\infty}^{\infty} I_j(\omega) e^{-i\omega(t-t')} d\omega. \quad (6.22)$$

We can find the function  $I_f(\omega)$  by using Eq. (3.25) which in our case ( $\eta = -1$ ) is of the form

$$G_j(\omega + i\epsilon) - G_j(\omega - i\epsilon) = -i(e^{\frac{\omega}{\theta}} + 1) I_j(\omega),$$

and using the  $\delta$ -function representation (3.27); the result is

$$I_j(\omega) = \frac{1}{2} \left(1 + \frac{T_j}{\omega_j}\right) \frac{\delta(\omega - \omega_j)}{1 + e^{\frac{\omega_j}{\theta}}} + \frac{1}{2} \left(1 - \frac{T_j}{\omega_j}\right) \frac{\delta(\omega + \omega_j)}{1 + e^{-\frac{\omega_j}{\theta}}} \quad (6.23)$$

We get from Eq. (6.22), putting  $t = t'$  in it, for the average occupation number  $\bar{n}_f$

$$\bar{n}_j = \frac{1}{2} \left\{ 1 - \frac{T_j}{\omega_j} \tanh \frac{\omega_j}{2\theta} \right\}. \quad (6.24)$$

Taking (6.15), (3.7a), (3.25), and (3.27) into account we get for the time correlation function the spectral expansion

$$\langle a_j^\dagger(t') a_{-j}^-(t) a_{-j'}^-(t) a_{j'}(t) \rangle = A_{j'} A_j(t-t')$$

$$= A_{j'} \int_{-\infty}^{\infty} \tilde{I}_j(\omega) e^{-i\omega(t-t')} d\omega, \quad (6.25)$$

where the spectral intensity  $\tilde{I}_f(\omega)$  is equal to

$$\tilde{I}_j(\omega) = \frac{L_j}{2\omega_j} \left\{ \frac{\delta(\omega - \omega_j)}{1 + e^{\frac{\omega_j}{\theta}}} - \frac{\delta(\omega + \omega_j)}{1 + e^{-\frac{\omega_j}{\theta}}} \right\}. \quad (6.26)$$

Putting  $t = t'$  into Eq. (6.25) we find the quantity  $A_j$

$$A_j = \int_{-\infty}^{\infty} \tilde{I}_j(\omega) d\omega = -\frac{L_j}{2\omega_j} \tanh \frac{\omega_j}{2\theta}. \quad (6.27)$$

One checks easily that Eqs. (6.27) and (6.24) satisfy also Eq. (6.17) and the assumptions made turn thus out to be valid. We get from (6.27) and (6.18) for the quantity  $L_f$  which plays the role of the gap in the spectrum of elementary excitations the equation

$$L_f = \frac{1}{V} \sum_g J(f, g) \frac{L_g}{2\omega_g} \tanh \frac{\omega_g}{2\theta}. \quad (6.28)$$

Equation (6.28) has a non-trivial solution  $L_f \neq 0$  at sufficiently low temperatures  $\theta$  for a positive definite kernel  $J(\mathbf{k}, \mathbf{k}')$  [see (6.3)] which corresponds to the prevailing of the attraction between electrons with opposite momenta and spins, which arises from the exchange of phonons, over the Coulomb repulsion. (For a study of the influence of the Coulomb interaction see reference 37.)

See reference 30 for the solution of Eq. (6.28) for the case where the kernel of the integral equation factorizes and reference 36 for more general assumptions about the kernel (see Sec. 6.4).

We can use (6.15) to get for the average energy

$$\langle H \rangle = \sum_f T_f \bar{n}_f - \frac{1}{2V} \sum_{f, f'} J(f, f') A_f A_{f'} \quad (6.29)$$

or, using (6.27) and (6.24)

$$\langle H \rangle = \frac{1}{2} \sum_f T_f \left( 1 - \frac{T_f}{\omega_f} \tanh \frac{\omega_f}{2\theta} \right)$$

$$- \frac{1}{2V} \sum_{f, f'} J(f, f') \frac{L_f}{2\omega_f} \tanh \frac{\omega_f}{2\theta} \frac{L_{f'}}{2\omega_{f'}} \tanh \frac{\omega_{f'}}{2\theta}. \quad (6.30)$$

Summing over  $f'$  in the second term of Eq. (6.30) and taking (6.28) into account we get finally

$$\langle H \rangle = \frac{1}{2} \sum_f T_f \left( 1 - \frac{T_f}{\omega_f} \tanh \frac{\omega_f}{2\theta} \right) - \frac{1}{2} \sum_f \frac{L_f^2}{2\omega_f} \tanh \frac{\omega_f}{2\theta}. \quad (6.31)$$

At zero temperature, the state with  $L_f \neq 0$  corresponds to a lower value of the energy, i.e., it is energetically more advantageous than the state with  $L_f = 0$  [the trivial solution of Eq. (6.31)]. We shall verify in the following (Sec. 6.5) that the trivial solution is impossible at temperatures below critical.

Using Eqs. (6.26) and (6.27), we find for the time correlation functions the expressions

$$\langle a_j^\dagger(t') a_j(t) \rangle = \frac{1}{2} \left( 1 + \frac{T_j}{\omega_j} \right) \frac{e^{-i\omega_j(t-t')}}{1 - e^{\frac{\omega_j}{\theta}}} + \frac{1}{2} \left( 1 - \frac{T_j}{\omega_j} \right) \frac{e^{i\omega_j(t-t')}}{1 + e^{-\frac{\omega_j}{\theta}}}, \quad (6.32)$$

$$\langle a_j^\dagger(t'), a_{-j}^-(t) a_{-j'}^-(t) a_{j'}(t) \rangle$$

$$= A_j A_{j'} \cos \omega_j(t-t') \left\{ 1 + i \frac{\tanh \omega_j(t-t')}{\tanh \frac{\omega_j}{2\theta}} \right\}. \quad (6.33)$$

The correlation function (6.33) vanishes for a perfect gas. Correlations of this kind which are typical for superconductivity are connected with the interaction. The time correlation functions (6.32) and (6.33) oscillate as  $t - t' \rightarrow \infty$  as in the case of the perfect gas. If one takes into account, however, the dropped asymptotically small terms, there appears in higher orders in the correlation functions an asymptotically small damping which tends to zero as  $V \rightarrow \infty$  ( $V/N = \text{const}$ ).

### 6.3. The Canonical Transformation Method

It is of some interest to compare for this model example the Green function method given here and N. N. Bogolyubov's method of the canonical u, v transformation, which was applied to problem under discussion in a paper by N. N. Bogolyubov, Yu. A. Tserkovnikov, and the present author.

Following the method of that paper, we introduce some ordinary functions  $A_f$  and write the Hamiltonian (6.1) in the form

$$\mathcal{H} = U + H_0 + H_1, \quad (6.34)$$

where

$$U = \frac{1}{2V} \sum_{f, f'} J(f, f') A_f A_{f'}, \quad (6.34a)$$

$$H_0 = \sum_f H_f = \sum_f \left\{ T_f a_f^\dagger a_f + \frac{1}{2} C_f (a_f^\dagger a_{-f} + a_{-f} a_f) \right\} \quad (6.34b)$$

$$H_1 = -\frac{1}{2V} \sum_{f, f'} J(f, f') B_f B_{f'}, \quad (6.34c)$$

$$B_f = a_{-f} a_f - A_f \quad (6.34d)$$

and where we have introduced the notation

$$C_f = -\frac{1}{V} \sum_{f'} J(f, f') A_{f'}. \quad (6.35)$$

The operator  $H_0$  is quadratic in the operators  $a_f$  and  $a_f^\dagger$ , and it can therefore be diagonalized by a canonical transformation

$$a_f = u_f \alpha_f + v_f \alpha_{-f}^\dagger, \quad (6.36)$$

$$u_f^2 + v_f^2 = 1, \quad u_f = u_{-f}, \quad v_f = -v_{-f} \quad (6.37)$$

( $u_f$  and  $v_f$  real).

We have then

$$T_f u_f v_f + \frac{C_f}{2} (u_f^2 - v_f^2) = 0, \quad (6.38)$$

whence we get, using (6.37),

$$u_f^2 = \frac{1}{2} \left( 1 + \frac{T_f}{\epsilon_f} \right), \quad v_f^2 = \frac{1}{2} \left( 1 - \frac{T_f}{\epsilon_f} \right), \quad u_f v_f = -\frac{C_f}{2\epsilon_f}, \quad (6.39)$$

where

$$\epsilon_f = \sqrt{T_f^2 + C_f^2} \quad (6.40)$$

and

$$H_0 = \sum_f \{ T_f v_f^2 + C_f u_f v_f \} + \sum_f \epsilon_f a_f^\dagger a_f. \quad (6.41)$$

We note that the operators  $H_f$ ,  $B_f$ , and  $B_f^\dagger$  commute with one another for different  $f$ .

We choose  $A_f$  from the condition

$$\langle B_f \rangle = 0, \quad (6.42)$$

where the averaging is over a grand canonical ensemble with Hamiltonian  $H_0$ . (We retain for such an average the earlier notation  $\langle \dots \rangle$ .)

We have then

$$\left. \begin{aligned} A_f = \langle a_{-f} a_f \rangle &= u_f v_f (1 - 2v_f) = -\frac{C_f}{2\epsilon_f} \tanh \frac{\epsilon_f}{2\theta}, \\ v_f = \langle a_f^\dagger a_f \rangle &= \{ 1 + e^{\frac{\epsilon_f}{\theta}} \}^{-1} \end{aligned} \right\} \quad (6.43)$$

and the contribution from the operator  $H_1$  becomes negligibly small as  $V \rightarrow \infty$  in comparison with the contributions from  $U + H_0$  (see reference 32 for details).

Using (6.35), (6.43), and (6.42) we get for  $C_f$  the equation

$$C_f = \frac{1}{2V} \sum_{f'} J(f, f') \tanh \frac{\epsilon_{f'}}{2\theta} \frac{C_{f'}}{\epsilon_{f'}}. \quad (6.44)$$

Comparing (6.20), (6.27), and (6.28) with (6.40), (6.43), and (6.44) we satisfy ourselves that

$$C_f = L_f, \quad A_f = A_{f'}, \quad \epsilon_f = \omega_f. \quad (6.45)$$

There is thus complete agreement between the method of the preceding subsection and that of the canonical transformation, and they lead to the same solutions. We get for the thermodynamic potential

$$\Omega = -\theta \ln \text{Sp} \left\{ e^{-\frac{U+H_0}{\theta}} \right\} = \sum_k T_k \left( 1 - \frac{T_k}{\epsilon_k} \right) - \sum_k \frac{C_k^2}{2\epsilon_k} \tanh \frac{\epsilon_k}{2\theta} - 2\theta \sum_k \ln \{ 1 + e^{\frac{\epsilon_k}{\theta}} \}, \quad (6.46)$$

where we have replaced  $f$  by  $k$  since here all quantities are spin-independent, and using (6.37) we have

$$C_f = (-1)^{\sigma - \frac{1}{2}} C_k.$$

One notices easily that the thermodynamic potential (6.46) is a minimum in the variables  $u_f$  and  $v_f$ , as should be the case for the exact solution. In calculating the entropy we need therefore only take into account the explicit dependence of  $\Omega$  on the temperature  $\theta$ , as terms that correspond to the temperature-dependence of  $u_f$  and  $v_f$  automatically drop out. We get thus an expression for the entropy, which is formally the same as the entropy of a perfect gas of elementary excitations

$$S = -\frac{\partial \Omega}{\partial \theta} = -2 \sum_k \{ v_k \ln v_k + (1 - v_k) \ln (1 - v_k) \}. \quad (6.47)$$

Such a simple formula occurs only for the distribution function of the elementary excitations  $\nu_k$ , but not for the real momentum distribution function (6.24).

The method of the canonical  $u, v$  transformation allowed us thus to evaluate asymptotically exactly the thermodynamic potential and the entropy of the system. The Green function method gives the average energy from which one can afterwards reduce also the other thermodynamic functions.

We note one interesting fact. It follows from Eq. (6.43) that

$$\langle a_{-f}, a_f \rangle \quad (6.48)$$

is a finite quantity. On the other hand, if we averaged over an ensemble, not with  $H_0$  but with the total Hamiltonian  $\mathcal{H}$ , the analogous quantity would be equal to zero. Indeed, the operator of the total number of particles

$$N = \sum_f a_f^\dagger a_f$$

commutes with  $\mathcal{H}$ , i.e., it is an integral of motion. Its eigenvalues  $N = 0, 1, 2, \dots$  are thus quantum numbers which number the eigenvalues of  $\mathcal{H}$ . Writing (6.48) in explicit form

$$\langle a_{-f}, a_f \rangle = Q^{-1} \sum_{\alpha, N} e^{-\frac{E_{\alpha, N}}{\theta}} C_{\alpha, N}^* a_{-f} a_f C_{\alpha, N}, \quad (6.49)$$

where  $E_{\alpha, N}$  and  $C_{\alpha, N}$  are the eigenvalues and eigenfunctions of the Hamiltonian  $\mathcal{H}$  corresponding to a

fixed  $N$ , we verify that this quantity is, indeed, equal to zero, since the operator  $a_{\alpha}^{\dagger} a_{\alpha}$  has no diagonal elements in the representation with fixed  $N$ ,

$$C_{\alpha, N}^* a_{\alpha}^{\dagger} C_{\alpha N} = 0.$$

To prove this it is essential that  $N$  be an exact integral of motion. For the operator  $H_0$  [see (6.34b)] the particle number operator  $N$  is no longer an exact integral of motion and the quantity (6.48) does therefore not vanish.

#### 6.4. The Solution of the Equations

We shall follow reference 36 and give the solution of the integral equation (6.44). We rewrite Eq. (6.44) in integral form

$$C(\xi) = \varrho \int_0^{\infty} d\xi' I\left(\frac{\xi}{\omega}, \frac{\xi'}{\omega}\right) \tanh\left(\frac{\varepsilon(\xi')}{2\theta}\right) \frac{C(\xi')}{\varepsilon(\xi')}, \quad (6.50)$$

where

$$I\left(\frac{\xi}{\omega}, \frac{\xi'}{\omega}\right) = J^{-1} \frac{1}{2} \int_{-1}^1 dt J(k, k') \left(t = \frac{kk'}{kk}\right),$$

$$\varrho = \frac{J}{2\pi^2} \left(k^2 \frac{dk}{d\xi}\right)_{k=k_0} = J \frac{mk_0}{2\pi^2}, \quad \xi = T_k = \frac{k^2}{2m} - \mu.$$

We choose the constant  $J > 0$  such that  $I(0, 0) = 1$ ,  $k_0$  is the Fermi momentum, and  $\omega$  is a characteristic energy (of the order of magnitude of the energy corresponding to the Debye limit of the phonon energies) for which the kernel  $J(\xi, \xi')$  is essentially different from zero. We assume that  $\omega$  is appreciably less than the Fermi energy and we remove from under the integral sign the slowly changing function  $k(\xi) = \sqrt{2m(\mu + \xi)}$  at the point  $\xi = 0$  [ $k(0) = k_0$ ].

We introduce a new unknown function  $\varphi(x)$  ( $x = \xi/\omega$ )

$$C(x) = C\varphi(x), \quad \varphi(0) = 1, \quad C = C(0) \quad (6.51)$$

and write Eq. (6.50) in the form

$$\left. \begin{aligned} \varphi(x) &= \varrho \int_0^{\infty} dx' I(x, x') \tanh \frac{\varepsilon(x') \varphi(x')}{\alpha \varepsilon(x')}, \\ \varepsilon(x) &= \sqrt{x^2 + \beta^2 \varphi^2(x)}, \quad \alpha = \frac{2\theta}{\omega}, \quad \beta = \frac{C}{\omega}. \end{aligned} \right\} \quad (6.52)$$

When solving the non-linear integral equation (6.52) we use the fact that it has a logarithmic singularity as  $x' \rightarrow 0$ ,  $\alpha \rightarrow 0$ , and  $\beta \rightarrow 0$ , and these parameters can be assumed to be very small ( $\alpha \ll 1$ ,  $\beta \ll 1$ ). For  $x = 0$  we get from (6.52) a transcendental equation for  $\alpha$  and  $\beta$

$$1 = \varrho \int_0^{\infty} dx I(0, x) \tanh \frac{\varepsilon(x) \varphi(x)}{\alpha \varepsilon(x)}. \quad (6.53)$$

To solve it we must still know the function  $\varphi(x)$ . To find an approximate equation for  $\varphi(x)$  with  $\alpha \ll 1$  and  $\beta \ll 1$ , we subtract from Eq. (6.52) Eq. (6.53) multiplied by  $I(x, 0)$ , and since the resultant equation should no longer have a singularity, we can let  $\alpha$  and

$\beta$  tend to zero. We then obtain for  $\varphi(x)$  the inhomogeneous Fredholm integral equation

$$\varphi(x) = I(x, 0) + \varrho \int_0^{\infty} \{I(x, x') - I(x, 0)I(0, x')\} \varphi(x') \frac{dx'}{x'}, \quad (6.54)$$

which no longer contains a singularity and is independent of the parameters  $\alpha$  and  $\beta$ . One easily obtains a solution of Eq. (6.53) as a power series in  $\rho$  by iteration. One can thus consider  $\varphi(x)$  to be a known function. If the kernel factorizes

$$I(x, x') = I(x, 0)I(x', 0) \quad (6.55)$$

we get as the exact solution of Eq. (6.54)

$$\varphi(x) = I(x, 0). \quad (6.56)$$

In the particular case of the Bardeen-Cooper-Schrieffer model interaction<sup>30</sup> we have

$$I(x, 0) = \begin{cases} 1 & \text{if } -\frac{\omega}{\mu} \leq x \leq \frac{\omega}{\mu}, \\ 0 & \text{outside this interval.} \end{cases} \quad (6.57)$$

We can simplify (6.53) by using the fact that  $\alpha$  and  $\beta$  are small and that there is a logarithmic singularity. To do this we integrate by parts and put  $\alpha = \beta = 0$  in the terms which do not contain a singularity (when taking the limit we assume  $\beta/\alpha = a = \text{const}$ ). We get then<sup>36</sup>

$$\begin{aligned} -\frac{1}{\varrho} &= \ln a \tanh a + \ln \alpha + \int_a^{\infty} \ln(x + \sqrt{x^2 - a^2}) \cosh^{-2} x dx \\ &+ \int_0^{\infty} \ln 2x \frac{d}{dx} \{I(x, 0) \varphi(x)\} dx. \end{aligned} \quad (6.58)$$

Equation (6.58) determines  $\beta$  as a function of  $\alpha$ , i.e., the temperature dependence of the energy gap  $C$ . At zero temperature  $\alpha = 0$  and we get N. N. Bogolyubov's solution<sup>31</sup>

$$\beta_0 = \frac{C}{\omega} = \exp \left\{ -\frac{1}{\varrho} - \int_0^{\infty} \ln 2x \frac{d}{dx} \{I(x, 0) \varphi(x)\} dx \right\}, \quad (6.59)$$

where

$$I(x, x') = J^{-1} \int_0^{q_0} \frac{g^2 u^2 du}{2u + x + x'}, \quad (6.60)$$

$\omega = \frac{1}{2} \omega_{q|q=k_0}$ ,  $q_0$  is the maximum Debye momentum, and  $g$  is a coupling constant [see (8.2) below]. At a temperature equal to the critical temperature,  $\theta = \theta_0$ , the gap in the spectrum of elementary excitations tends to zero ( $\beta = 0$  or  $\alpha = 0$ ) and we find from Eq. (6.58) the following expression for  $\theta_0$ <sup>36</sup>

$$\begin{aligned} \alpha_0 = \frac{2\theta_0}{\omega} &= \exp \left\{ -\frac{1}{\varrho} - \int_0^{\infty} \ln x \cosh^{-2} x dx \right. \\ &\left. - \int_0^{\infty} \ln x \frac{d}{dx} [I(0, x) \varphi(x)] dx \right\}. \end{aligned} \quad (6.61)$$

The ratio of the critical temperature to the magnitude

of the gap at zero temperature and also the relative jump in the heat capacity are independent of the function  $\varphi$  and are the same as the expressions obtained in reference 30 with the simplified interaction (6.55). These properties are thus not connected with the detailed form of the interaction, but only with the singularity of the integral equations.

### 6.5. Instability of the Trivial Solution

The non-trivial solution  $A_f \neq 0$  and  $C_f \neq 0$  corresponds for  $\theta < \theta_0$  to a lower value of the thermodynamic potential (6.46), i.e., is thermodynamically more stable than the trivial solution  $A_f = 0$ . This, however, is not the whole story. We shall show that below the critical temperature the trivial solution  $A_f = 0$  is impossible.\* Indeed, assuming that

$$\langle a_g^* a_{-g}^* a_{-j} a_j \rangle = 0 \quad \text{or} \quad A_j = 0,$$

we get, retaining in the second of Eqs. (6.14) also the inhomogeneous term,

$$(E - 2T_{j'} + T_j) \Gamma_{j'j} = \frac{\bar{n}_j}{2\pi} (\delta_{j-j'} - \delta_{j+j'}) - \frac{1-2\bar{n}_{j'}}{V} \sum_g J(j', g) \Gamma_{jg} - \frac{1}{V} \sum_g J(j', g) \Gamma_{jg} (\delta_{j+j'} + \delta_{j-j'}). \quad (6.62)$$

We find the pole of the Green function  $\Gamma_{ff'}$  from the condition that the homogeneous part of Eq. (6.62) should tend to zero, i.e.,

$$(E - 2T_{j'} + T_j) \Gamma_{j'j} + \frac{1-2\bar{n}_{j'}}{V} \sum_g J(j', g) \Gamma_{jg} = 0, \quad (6.63)$$

where we have dropped asymptotically small terms. The index  $f$  in Eq. (6.63) can be chosen freely, and if we choose it so that  $T_f = 0$  and introduce the notation

$$\Phi_{j'} = \Gamma_{j'j}, \quad (6.64)$$

we get for  $\Phi_f$  the equation

$$(E - 2T_j) \Phi_j = - \frac{1-2\bar{n}_j}{V} \sum_{j'} J(j, j') \Phi_{j'}. \quad (6.65)$$

If we use the method used in reference 36, we can solve the integral Eq. (6.65).

Introducing the notation

$$\mathcal{F}_j = - \frac{1}{V} \sum_{j'} J(j, j') \Phi_{j'}, \quad (6.66)$$

we can write Eq. (6.65) in the form

$$(E - 2T_j) \Phi_j = (1 - 2\bar{n}_j) \mathcal{F}_j. \quad (6.67)$$

Substituting into Eq. (6.66)  $\Phi_f$  from Eq. (6.67) we get

$$\mathcal{F}_k = \frac{1}{2V} \sum_{k'} J(k, k') \frac{\tanh \frac{T_{k'}}{2\theta}}{T_{k'} - \frac{E}{2}} \mathcal{F}_{k'}, \quad (6.68)$$

where we have changed  $f = (k, \sigma)$  to  $k$ .

\*Considerations of the impossibility of two solutions (a trivial one and a non-trivial one) at  $\theta < \theta_0$  were given by G. Wentzel,<sup>70</sup> who showed that the thermodynamic potential must by definition be a single-valued function.

Changing the sum to an integral and introducing dimensionless variables  $x = \xi/\omega$  and a new function  $f(x)$

$$\mathcal{F}(x) = \mathcal{F}(0) f(x) \quad (f(0) = 1), \quad (6.69)$$

we get for it the equation

$$f(x) = \varrho \int_0^\infty I(x, x') \tanh \frac{x'}{\alpha} \frac{2x'}{x'^2 - \gamma^2} f(x') dx', \quad (6.70)$$

where  $\gamma = E/2\omega$  is a dimensionless parameter which is assumed to be small ( $\gamma \ll 1$ ); the rest of the notation is the same as in (6.50) to (6.52).

Equation (6.70) is a homogeneous Fredholm integral equation with singularities of a logarithmic character as  $\alpha \rightarrow 0$  and  $\gamma \rightarrow 0$ .

One can write the equation for  $f(x)$  in the form of an inhomogeneous Fredholm integral equation by separating from it the terms with singularities and, using the fact that  $\alpha$  and  $\gamma$  are small, going to the limit  $\alpha \rightarrow 0$ ,  $\gamma \rightarrow 0$  in the terms which do not contain singularities. [we used the same procedure earlier on with Eq. (6.52).] We get in this way

$$f(x) = I(x, 0) + \varrho \int_0^\infty \{I(x, x') - I(x, 0)I(0, x')\} f(x') \frac{dx'}{x'}. \quad (6.71)$$

Comparing (6.71) with (6.54) we see that

$$f(x) = \varphi(x). \quad (6.72)$$

We find the parameter  $\gamma^2$  as a function of  $\alpha$  from the transcendental equation

$$1 = \varrho \int_0^\infty I(0, x) \tanh \frac{x}{\alpha} \frac{x}{x^2 - \gamma^2} \varphi(x) dx. \quad (6.73)$$

For instance, for  $\alpha = 0$ , we integrate (6.70) by parts and get

$$\frac{2}{\varrho} = - \ln(-\gamma^2) - \int_0^\infty \ln(x^2 - \gamma^2) \frac{d}{dx} \{\varphi(x) I(0, x)\} dx. \quad (6.74)$$

Taking in the second integral the limit  $\gamma \rightarrow 0$  we get

$$\gamma^2 = \left(\frac{E}{2\omega}\right)^2 = - \exp \left\{ - \frac{2}{\varrho} - 2 \int_0^\infty \ln x \frac{d}{dx} \{\varphi(x) I(0, x)\} dx - \frac{C^2(0)}{4\omega^2} \right\} < 0. \quad (6.75)$$

The denominator of the Green function tends to zero in the points  $E = \pm iC(0)$ .

Starting from the equation  $A_f = 0$ , i.e., from the existence of the trivial solution, we have thus found that the Green function has a singularity in the complex plane outside the real axis; since, however, it must be analytic everywhere outside the real axis, such solutions cannot occur, and hence  $A_f \neq 0$ . At the critical temperature the complex root vanishes and we have the solution  $E = 0$ . Indeed, putting  $\gamma = 0$  in Eq. (6.73) we get Eq. (6.53) for  $\beta = 0$ , which defines the critical temperature.

The application of Green functions thus enabled us, without any other considerations, to choose from the two solutions the only one which is physically acceptable.



## 7. APPLICATION TO THE THEORY OF FERROMAGNETISM

N. N. Bogolyubov and S. V. Tyablikov,<sup>19</sup> and also S. V. Tyablikov,<sup>38</sup> have applied advanced and retarded Green functions to the thermodynamics of ferromagnetics. We shall follow their papers.

According to the Heisenberg model, a ferromagnetic crystal can be described by a Hamiltonian expressed in terms of spin operators

$$\mathcal{H} = -\mu_B H \sum_f S_f^z - \frac{1}{2} \sum_{f_1 f_2} J(f_1 - f_2) S_{f_1}^\alpha S_{f_2}^\alpha, \quad (7.1)$$

where  $S_f^\alpha$  is the  $\alpha$  component of the spin of an electron situated at the lattice site  $f$ ,  $J(f_1 - f_2)$  is the exchange integral which we shall assume to be positive,  $H$  is the external magnetic field which is parallel to the  $z$ -axis, and  $\mu_B$  is the Bohr magneton. The summation is over lattice sites with different  $f$ , so that we can put  $J(0) = 0$ . We shall assume, moreover, that there is one electron on each lattice site.

Changing in the Hamiltonian (7.1) from spin operators to Pauli operators

$$\left. \begin{aligned} S_f^x &= b_f + b_f^\dagger, \\ S_f^y &= i(b_f^\dagger - b_f), \\ S_f^z &= 1 - 2b_f^\dagger b_f, \end{aligned} \right\} \quad (7.2)$$

which satisfy the commutation relations

$$\left. \begin{aligned} b_f b_f^\dagger + b_f^\dagger b_f &= 1, & b_f^2 &= (b_f^\dagger)^2 = 0, \\ b_f b_g^\dagger - b_g^\dagger b_f &= 0, \\ b_f b_g - b_g b_f &= b_f^\dagger b_g^\dagger - b_g^\dagger b_f^\dagger = 0 \end{aligned} \right\} \text{ if } f \neq g, \quad (7.3)$$

which are easily checked by direct substitution. The commutation relations for the Pauli operators are of the Fermi type for the same lattice sites and of the Bose type for different sites. The Hamiltonian (7.1) assumes upon transformation the form

$$\mathcal{H} = -N \left( \mu_B H + \frac{J(0)}{2} \right) + (2\mu_B H + 2J(0)) \sum_f b_f^\dagger b_f - \sum_{f_1 f_2} 2J(f_1 - f_2) b_{f_1}^\dagger b_{f_2} - \sum_{f_1 f_2} 2J(f_1 - f_2) n_{f_1} n_{f_2}, \quad (7.4)$$

where  $J(0) = \sum_f J(f)$ , and  $N$  the number of lattice sites. The operator  $n_f$ ,

$$n_f = b_f^\dagger b_f \quad (7.5)$$

is the number of electrons with "left hand" spins at the site  $f$ . The average number of "left hand" spins at any lattice site

$$\bar{n} = \langle n_f \rangle \quad (7.6)$$

is independent of  $f$  because of the translational symmetry and the equivalence of all lattice sites. Moreover, it follows from the equations of motion for  $n_f$  that

$$\left\langle \frac{dn_f}{dt} \right\rangle = \frac{d\bar{n}}{dt} = 0. \quad (7.7)$$

The operators  $b_g$  and  $n_g$  satisfy the equations of motion

$$\begin{aligned} i \frac{db_g}{dt} &= [2\mu_B + 2J(0)] b_g + \sum_p 2J(g-p) b_p \\ &+ \sum_p 4J(g-p) (n_p b_p - b_p n_p), \\ i \frac{dn_g}{dt} &= -2 \sum_p J(g-p) (b_g^\dagger b_p - b_p^\dagger b_g). \end{aligned} \quad (7.8)$$

We introduce the Green functions ( $\eta = 1$ )

$$\begin{aligned} G_{g,f}(t-t') &= \langle \langle b_g(t); b_f^\dagger(t') \rangle \rangle, \\ G_{g_1 g_2, f}(t-t') &= \langle \langle n_{g_1}(t) b_{g_2}(t); b_f^\dagger(t') \rangle \rangle. \end{aligned} \quad (7.9)$$

Using (7.8) we get for  $G_{g,f}$  the equation

$$\begin{aligned} i \frac{dG_{g,f}}{dt} &= (1 - 2\bar{n}) \delta(t-t') + [2\mu_B H + 2J(0)] G_{g,f} \\ &- \sum_p 2J(g-p) G_{p,f} + \sum_p 4J(g-p) (G_{g p, f} - G_{p g, f}). \end{aligned} \quad (7.10)$$

In the following we shall restrict ourselves to the first-order approximation and we shall decouple the chain of equations for the Green functions, taking

$$\begin{aligned} G_{g p, f}(t-t') &= \langle \langle n_g(t) b_p(t); b_f^\dagger(t') \rangle \rangle = \langle n_g \rangle \langle \langle b_p(t); b_f^\dagger(t') \rangle \rangle \\ &= \bar{n} G_{p, f}(t-t'). \end{aligned} \quad (7.11)$$

In that case Eq. (7.10) is of the form

$$\begin{aligned} i \frac{dG_{g,f}}{dt} &- [2\mu_B H + (1 - 2\bar{n}) 2J(0)] G_{g,f} \\ &+ \sum_p (1 - 2\bar{n}) 2J(g-p) G_{p, f} = (1 - 2\bar{n}) \delta(t-t') \delta_{g,f} \end{aligned} \quad (7.12)$$

and it no longer contains higher Green functions.

The method of decoupling (7.11) corresponds to the method of approximate second quantization<sup>39</sup>, improved thermodynamically for the higher temperature region. Indeed, in the method of reference 39 the Pauli operators were assumed to be approximately Bose-operators and the last term in the Hamiltonian (7.4) was neglected, which corresponds to the low temperature region, well below the Curie temperature. In that approximation one must put in Eq. (7.12)  $\bar{n} = 0$ . When the temperature rises, the role of the terms containing a factor  $\bar{n}$  increases and one must by then take them into account.

We change now to the Fourier components of the Green functions

$$G_{g,f}(t) = \int_{-\infty}^{\infty} G_{g,f}(E) e^{-iEt} dE \quad (7.13)$$

and write Eq. (7.12) in the form

$$\begin{aligned} EG_{g,f} &= \frac{1}{2\pi} (1 - 2\bar{n}) \delta_{g,f} + [2\mu_B H + (1 - 2\bar{n}) 2J(0)] G_{g,f} \\ &- \sum_p (1 - 2\bar{n}) 2J(g-p) G_{p, f}. \end{aligned} \quad (7.14)$$

One can solve Eq. (7.14) by the usual method applied in the theory of ferromagnetism and based upon the

translational symmetry of the lattice. Taking into account that then  $G_{\mathbf{g},\mathbf{f}}$  depends only on the difference of the lattice vectors  $\mathbf{g}-\mathbf{f}$  and is a periodic function we change to the Fourier components in these variables

$$G_{\mathbf{g},\mathbf{f}}(E) = \frac{1}{N} \sum_{\mathbf{q}} e^{i(\mathbf{g}-\mathbf{f},\mathbf{q})} G_{\mathbf{q}}(E) \quad (\mathbf{q} - \text{wave vector}). \quad (7.15)$$

The Kronecker symbol  $\delta_{\mathbf{g},\mathbf{f}}$  can also be written in the form

$$\delta_{\mathbf{g},\mathbf{f}} = \frac{1}{N} \sum_{\mathbf{q}} e^{i(\mathbf{g}-\mathbf{f},\mathbf{q})}. \quad (7.16)$$

Substituting (7.15) and (7.16) into Eq. (7.14) we get

$$G_{\mathbf{q}}(E) = \frac{1}{2\pi} \frac{1-2\bar{n}}{E-E_{\mathbf{q}}}, \quad (7.17)$$

where

$$E_{\mathbf{q}} = 2\mu_B H + (1-2\bar{n})2(\mathcal{J}(0) - \mathcal{J}(\mathbf{q})), \quad (7.18)$$

$$\mathcal{J}(\mathbf{q}) = \sum_{\mathbf{f}} J(\mathbf{f}) e^{i(\mathbf{f},\mathbf{q})}. \quad (7.19)$$

Using (3.25) and (3.27) for the spectral intensity we find

$$\left. \begin{aligned} I_{\mathbf{q}}(\omega) &= \frac{1-2\bar{n}}{e^{E_{\mathbf{q}}/\theta} - 1} \delta(\omega - E_{\mathbf{q}}), \\ I_{\mathbf{g},\mathbf{f}}(\omega) &= \frac{1}{N} \sum_{\mathbf{q}} e^{i(\mathbf{g}-\mathbf{f},\mathbf{q})} I_{\mathbf{q}}(\omega) \\ &= \frac{1}{N} \sum_{\mathbf{q}} \frac{1-2\bar{n}}{e^{E_{\mathbf{q}}/\theta} - 1} e^{i(\mathbf{g}-\mathbf{f},\mathbf{q})} \delta(\omega - E_{\mathbf{q}}). \end{aligned} \right\} \quad (7.20)$$

We have thus from (3.7a)

$$\begin{aligned} \langle b_{\mathbf{f}}(t') b_{\mathbf{g}}(t) \rangle &= \int_{-\infty}^{\infty} I_{\mathbf{g},\mathbf{f}}(\omega) e^{-i\omega(t-t')} d\omega \\ &= \frac{1}{N} \sum_{\mathbf{q}} e^{i(\mathbf{g}-\mathbf{f},\mathbf{q})} e^{-iE_{\mathbf{q}}(t-t')} \frac{1-2\bar{n}}{e^{E_{\mathbf{q}}/\theta} - 1}. \end{aligned}$$

Putting here  $t' = t$ ,  $\mathbf{f} = \mathbf{g}$ , and changing from a sum

$$\sigma = \begin{cases} 1 - \sum_{j \geq 3} A_j \tau^j, & \tau < \tau_c \\ \sqrt{\frac{3}{\tau} \left(1 - \frac{\tau}{\tau_c}\right)} \left\{ 1 + \frac{1}{20} \frac{3}{\tau} \left(1 - \frac{\tau}{\tau_c}\right) + 5 \cdot 10^{-4} \left[ \frac{3}{\tau} \left(1 - \frac{\tau}{\tau_c}\right) \right]^2 \right\}, & \tau \leq \tau_c \quad (\tau_c - \tau \ll 1), \quad h = 0, \\ \sigma = t_0 + t_0 (1 - t_0^2) \frac{1}{\tau} + t_0 (1 - t_0^2) \left( \frac{\nu-1}{\nu} - 2t_0^2 \right) \frac{1}{\tau^2}, & \tau > \tau_c, \end{cases} \quad (7.25a)$$

$$\left. \begin{aligned} & \tau \leq \tau_c \quad (\tau_c - \tau \ll 1), \quad h = 0, \\ & \tau > \tau_c, \end{aligned} \right\} \quad (7.25b)$$

$$\left. \begin{aligned} & \tau > \tau_c, \end{aligned} \right\} \quad (7.25c)$$

$$t_0 = \tanh \left( \frac{h}{\tau} \right), \quad c = \frac{\nu}{(2\pi)^3} \int \frac{d\mathbf{q}}{1-i(\mathbf{q})},$$

where  $\tau_c = \theta_c / \mathcal{J}(0) = 1/c$  is the dimensionless Curie temperature. For a simple cubic lattice  $c = 1.516$ ,  $\nu$  is the number of nearest neighbors in the lattice;  $A_f$  a function of  $h/\tau$ .

$$\left. \begin{aligned} A_3 &= \frac{2\nu}{(8\pi\alpha)^{3/2}} z_3 \left( \frac{h}{\tau} \right) \left( \frac{3}{4\pi} \right)^{3/2}, \quad A_4 = 0, \quad A_5 \neq 0; \quad A_6 \neq 0, \\ \alpha &= \frac{1}{6\mathcal{J}(0)} \sum_{\mathbf{f}} f^2 J(\mathbf{f}); \quad z_p = \sum_{n=1}^{\infty} n^{-p} \exp \left( -\frac{nh}{\tau} \right). \end{aligned} \right\} \quad (7.26)$$

over  $\mathbf{q}$  to an integral, we get for  $\bar{n}$  the transcendental equation<sup>19</sup>

$$\frac{\bar{n}}{1-2\bar{n}} = \frac{\nu}{(2\pi)^3} \int \frac{d\mathbf{q}}{e^{E_{\mathbf{q}}/\theta} - 1}, \quad (7.21)$$

where  $V = V/N$  is the volume of the elementary cell.

Equation (7.21) determines the relative magnetization  $\sigma$

$$\sigma = \langle S_z^c \rangle = 1 - 2\bar{n}. \quad (7.22)$$

Introducing the dimensionless variables

$$h = \frac{\mu_B H}{\mathcal{J}(0)}, \quad \tau = \frac{\theta}{\mathcal{J}(0)}, \quad i(\mathbf{q}) = \frac{\mathcal{J}(\mathbf{q})}{\mathcal{J}(0)} \quad (7.23)$$

( $h$  is the dimensionless magnetic field,  $\tau$  the dimensionless temperature, and  $i(\mathbf{q})$  the dimensionless exchange integral) we can write (7.21) in the form

$$\frac{1}{\sigma} = \frac{\nu}{(2\pi)^3} \int \coth \frac{h + \sigma(1-i(\mathbf{q}))}{\tau} d\mathbf{q}. \quad (7.24)$$

In the first approximation considered here, the Green function has a pole on the real axis for  $E = E_{\mathbf{q}}$ ; hence,  $E_{\mathbf{q}}$  is the energy of the elementary excitation of the spin wave, which depends through  $\sigma$  on the temperature, in contradistinction to the usual spin wave theory. In higher orders the pole disappears and there is damping. We shall consider the role of damping in Sec. 8 for the example of electrons interacting with the lattice.

Equation (7.24) is very interesting because it gives an interpolation formula for the magnetization  $\sigma$  for a wide range of temperatures for the case under consideration of a positive exchange integral. For negative values of the exchange integral the solution is unstable in sufficiently weak fields [the right hand side of (7.21) becomes negative, whereas  $\bar{n} > 0$ ].

Solving Eq. (7.24)<sup>20</sup> we get for the relative magnetization  $\sigma$  the formula

It follows from the transcendental Eq. (7.24) and Eqs. (7.25a, b, and c) that at temperatures below the Curie temperature  $\theta_c = \mathcal{J}(0)/c$  there occurs spontaneous magnetization, i.e.,  $\sigma \neq 0$  for  $H = 0$ , and the system is in a ferromagnetic state. At the Curie temperature, the spontaneous magnetization vanishes. For  $\theta > \theta_c$  the system goes over into a paramagnetic state. Equation (7.24) and Eqs. (7.25a, b, and c) describe this transition completely. We get as limiting cases all well-known results from the quantum theory of ferromagnetism.

Indeed, for  $\theta \leq \theta_c$  we get from (7.25a) Bloch's spin wave theory; near the Curie temperature  $\theta \lesssim \theta_c$  we get from (7.25b) the results of the molecular field theory, and for  $\theta > \theta_c$  from (7.25c) a theory of paramagnetism which is nearly the same as Opechowski's results, obtained by means of the thermodynamic perturbation theory (a difference occurs in the third term).

The authors of references 19 and 38 thus were able to improve substantially the quantum theory of ferromagnetism and to construct an equation for the magnetization, (7.24), which is suitable for all temperature ranges. (See references 41 and 42 for the first attempts in this direction.) Naturally, this equation has partly an interpolation character, but the agreement of the main terms at temperatures appreciably below the Curie temperature, in the neighborhood of the Curie temperature, and at temperatures appreciably higher than the Curie temperature with the well-known results of the spin-wave theory, the molecular-field theory, and the regularized perturbation theory shows that this interpolation is sufficiently flexible. In the very interesting paper by Dyson<sup>43</sup> on the theory of ferromagnetism he obtained  $A_4 = A_6 = 0$  which is different from (7.26). This shows apparently that one must take higher order Green functions into account to make the results more exact.

One can obtain the results of references 19 and 38 by establishing a chain of equations for Green functions which are built up directly from the spin operators.<sup>44</sup> The method of references 19 and 38 can also be applied to improve the quantum theory of antiferromagnetism<sup>44</sup> and the theory of magnetic anisotropy.<sup>45</sup>

## 8. ELECTRON-LATTICE INTERACTION

### 8.1. Electron-Lattice Interaction in a Metal

In the present section we shall consider a system of electrons interacting with the lattice phonons. We shall consider metals in the normal state, and following reference 19 restrict ourselves to the simplest approximation, which is insufficient to take effects such as superconductivity into account. This example, however, which has a methodological character, enables us to elucidate a number of important properties of a system of interacting particles, which will occur also in other systems, namely: the occurrence of damping and its influence on the distribution functions. A system of electrons interacting with phonons for the non-superconducting state at zero temperatures was considered by a Green function method in references 46 and 47, while in the last paper the role of damping was studied. (See references 31 and 64 for a theory of superconductivity based upon the Fröhlich Hamiltonian.) In the present section we shall follow reference 19, amplifying it by considering the phonon Green functions.

The system of electrons in a lattice is described by the Fröhlich Hamiltonian

$$\mathcal{H} = \sum_{k,\sigma} T_k a_{k\sigma}^\dagger a_{k\sigma} + \sum_q \omega_q b_q^\dagger b_q + \sum_{\substack{k_1, k_2, q \\ (k_1 - k_2 = q)}} A_q a_{k_1\sigma}^\dagger a_{k_2\sigma} (b_q + b_q^-), \quad (8.1)$$

where  $T_k = k^2/2m - \mu$ ,  $\mu$  is the chemical potential,  $\omega_q$  the energy of a phonon,  $a_{k\sigma}^\dagger$ ,  $a_{k\sigma}$ ,  $b_q^\dagger$ , and  $b_q$  the creation and annihilation operators of the electrons and phonons, respectively, and the function  $A_q$  describes the coupling of the electrons to the phonon field

$$A_q = g(q) \left( \frac{\omega_q}{2V} \right)^{\frac{1}{2}} \quad (g(q) = g(-q)). \quad (8.2)$$

The operators  $a_{k\sigma}^\dagger$ ,  $a_{k\sigma}$ ,  $b_q^\dagger$ , and  $b_q$  satisfy the equations of motion

$$\left. \begin{aligned} i \frac{da_{k\sigma}}{dt} &= T_k a_{k\sigma} + \sum_q A_q a_{k-q, \sigma} (b_q + b_q^-), \\ -i \frac{da_{k\sigma}^\dagger}{dt} &= T_k a_{k\sigma}^\dagger + \sum_q A_q a_{k+q, \sigma}^\dagger (b_q + b_q^-), \\ i \frac{db_q}{dt} &= \omega_q b_q + \sum_{k, \sigma} A_q a_{k-q, \sigma}^\dagger a_{k\sigma}, \\ -i \frac{db_q^-}{dt} &= \omega_q b_q^- + \sum_{k, \sigma} A_q a_{k+q, \sigma}^\dagger a_{k\sigma}. \end{aligned} \right\} \quad (8.3)$$

We introduce the single-particle Green functions of a fermion and a phonon type,  $G_k$  and  $G_p$  (in reference 19 only the fermion Green functions  $G_k$  were considered)

$$\left. \begin{aligned} G_k(t-t') &= \langle\langle a_{k\sigma}(t); a_{k\sigma}^\dagger(t') \rangle\rangle \quad (\eta = -1), \\ G_q(t-t') &= \langle\langle b_q(t); b_q^\dagger(t') \rangle\rangle \quad (\eta = 1) \end{aligned} \right\} \quad (8.4)$$

and we construct their equations of motion

$$\left. \begin{aligned} i \frac{dG_k}{dt} &= \delta(t-t') + T_k G_k + \sum_q A_q \langle\langle a_{k-q, \sigma} (b_q + b_q^-); a_{k\sigma}^\dagger(t') \rangle\rangle, \\ i \frac{dG_q}{dt} &= \delta(t-t') + \omega_q G_q + \sum_{k, \sigma} A_q \langle\langle a_{k-q, \sigma}^\dagger a_{k\sigma}; b_q^\dagger(t') \rangle\rangle. \end{aligned} \right\} \quad (8.5)$$

We see from Eqs. (8.5) that it is convenient to introduce mixed type Green functions, containing both Fermi-Dirac and Bose-Einstein operators,

$$\left. \begin{aligned} \Gamma_{k-q, q, h}(t-t') &= \langle\langle a_{k-q, \sigma}(t) b_q(t); a_{k\sigma}^\dagger(t') \rangle\rangle \quad (\eta = -1), \\ \Gamma_{k-q, q, h}^-(t-t') &= \langle\langle a_{k-q, \sigma}(t) b_q^-(t); a_{k\sigma}^\dagger(t') \rangle\rangle \quad (\eta = -1), \\ G_{k-q, h, q}(t-t') &= \langle\langle a_{k-q, \sigma}^\dagger(t) a_{k\sigma}(t); b_q^\dagger(t') \rangle\rangle \quad (\eta = 1). \end{aligned} \right\} \quad (8.6)$$

We get the following set of exact equations for the Green functions (8.4) and (8.6)

$$i \frac{dG_k}{dt} = \delta(t-t') + T_k G_k + \sum_q A_q (\Gamma_{k-q, q, h} + \Gamma_{k-q, q, h}^-), \quad (8.7a)$$

$$i \frac{dG_q}{dt} = \delta(t-t') + \omega_q G_q + \sum_{k, \sigma} A_q G_{k-q, h, q}, \quad (8.7b)$$

$$\begin{aligned} i \frac{d\Gamma_{k-q, q, h}}{dt} &= (T_{k-q} + \omega_q) \Gamma_{k-q, q, h} \\ &+ \sum_{q_1} A_{q_1} \langle\langle a_{k-q-q_1} (b_{q_1} + b_{q_1}^-) b_q; a_{k\sigma}^\dagger(t') \rangle\rangle \\ &+ \sum_{k_1 \sigma_1} A_{q_1} \langle\langle a_{k-q, \sigma} a_{k_1 - q, \sigma_1}^\dagger a_{k_1 \sigma_1}; a_{k\sigma}^\dagger(t') \rangle\rangle \end{aligned} \quad (8.7c)$$

$$i \frac{d\Gamma_{k-q, q, h}^1}{dt} = (T_{k-q} - \omega_q) \Gamma_{k-q, q, h}^1 + \sum_{q_1} A_{q_1} \langle \langle a_{k-q-q_1, \sigma} (b_{q_1} + b_{-q_1}^*) b_{-q}^*; a_{k\sigma}^*(t') \rangle \rangle - \sum_{k_1 \sigma_1} A_{q_1} \langle \langle a_{k-q, \sigma}, a_{k_1-q, \sigma_1}^* a_{k_1 \sigma_1}, a_{k\sigma}^*(t') \rangle \rangle, \quad (8.7d)$$

$$i \frac{dG_{k-q, h, q}}{dt} = (T_k - T_{k-q}) G_{k-q, h, q} + \sum_{q_1} A_{q_1} \langle \langle a_{k-q, \sigma}^* a_{k-q_1, \sigma} (b_{q_1}^* + b_{-q_1}^-); b_q^*(t') \rangle \rangle - \sum_{q_1} A_{q_1} \langle \langle a_{k-q+q_1, \sigma}^* (b_{q_1} + b_{-q_1}^-) a_{k\sigma}; b_q^*(t') \rangle \rangle. \quad (8.7e)$$

(The last three equations do not contain an inhomogeneous part, as  $q \neq 0$ .)

Apart from the introduced Green functions (8.4) and (8.6), Eqs. (8.7) contain also higher order Green functions, for which we should in turn construct equations of motion and continue the process further. We note

$$\left. \begin{aligned} \langle \langle a_{k-q-q_1, \sigma} (b_{q_1} + b_{-q_1}^-) b_q; a_{k\sigma}^*(t') \rangle \rangle &= \delta_{q+q_1} v_q G_k(t-t'), \\ \langle \langle a_{k-q, \sigma} a_{k_1-q_1, \sigma_1}^* a_{k_1 \sigma_1}; a_{k\sigma}^*(t') \rangle \rangle &= \delta_{k_1-k} \delta_{\sigma-\sigma_1} (1-n_{k-q}) G_k(t-t'), \\ \langle \langle a_{k-q-q_1, \sigma} (b_{q_1} + b_{-q_1}^-) b_{-q}^*; a_{k\sigma}^*(t') \rangle \rangle &= \delta_{q+q_1} (1+v_q) G_k(t-t'), \\ \langle \langle a_{k-q, \sigma}^* a_{k-q_1, \sigma} (b_{q_1} + b_{-q_1}^-); b_q^*(t') \rangle \rangle &= \delta_{q_1-q} n_{k-q} G_q(t-t'), \\ v_q &= \langle b_q^* b_q \rangle, \quad n_k = \langle a_{k\sigma}^* a_{k\sigma} \rangle. \end{aligned} \right\} \quad (8.8)$$

The approximation (8.8) is fairly coarse, and, in particular, it is insufficient to take into account the correlation between electrons which leads to the superconducting state<sup>30,31</sup> and which is important at low temperatures.\*

One might, without decoupling the Green functions (8.8), construct for them equations of motion and make an approximate decoupling for the higher order Green functions occurring in these equations. We shall not do that and we shall restrict ourselves to the simplest approximation (8.8) as it is sufficiently simple and reflects a number of interesting properties of a system of interacting particles. Using (8.8) we get an approximate set of equations for the Green functions

$$\left. \begin{aligned} i \frac{dG}{dt} &= \delta(t-t') + T_k G_k + \sum_q A_q (\Gamma_{k-q, q, k} + \Gamma_{k-q, q, k}^1), \\ i \frac{dG_q}{dt} &= \delta(t-t') + \omega_q G_q + \sum_{k, \sigma} A_q G_{k-q, k, q}, \\ i \frac{d\Gamma_{k-q, q, h}}{dt} &= (T_{k-q} + \omega_q) \Gamma_{k-q, q, h} + A_q (v_q + 1 - n_{k-q}) G_k, \\ i \frac{d\Gamma_{k-q, q, h}^1}{dt} &= (T_{k-q} - \omega_q) \Gamma_{k-q, q, h}^1 + A_q (n_{k-q} + v_q) G_k, \\ i \frac{dG_{k-q, h, q}}{dt} &= (T_k - T_{k-q}) G_{k-q, h, q} + A_q (n_{k-q} - n_k) G_q. \end{aligned} \right\} \quad (8.9)$$

\*Using the same method one can obtain the results of the theory of superconductivity if we consider also, when decoupling the Green functions (8.8), functions of the kind  $\langle \langle a_{k\sigma}(t); a_{-k, -\sigma}(t') \rangle \rangle$  (see reference 64), i.e., take into account the correlation between electrons with opposite momenta and spins.

that the energy can be expressed in the Green functions (8.4) and (8.6) only. If we decouple the chain of equations for the Green functions, (8.7), making some kind of approximation for the higher order Green functions, the inaccuracy introduced then will be the smaller the higher the order of the Green functions for which the decoupling is performed. It is, for instance, well known that in classical statistics a rather simple approximation for the tertiary correlation function describes approximately some properties of the liquid state.<sup>48,49</sup> For a system with a direct interaction the simplest way to decouple the chain, where the second correlation function is expressed in terms of the first one, leads to the Hartree-Fock method, and the corresponding approximation for the triple Green function leads to the generalized Fock method.<sup>18</sup>

We carry out the simplest interpolation decoupling of the higher Green functions occurring in Eqs. (8.7) by pairing off, where possible, operators referring to the same time

We note, however, that the first two equations of this set are exact. The set (8.9) is a broken-off chain of equations for the Green functions. Changing over to the Fourier components of the Green functions in these equations,

$$\left. \begin{aligned} G_k(t) &= \int_{-\infty}^{\infty} G_k(E) e^{-iEt} dE; \quad G_q(t) = \int_{-\infty}^{\infty} G_q(E) e^{-iEt} dE, \\ \Gamma_{k-q, q, h}(t) &= \int_{-\infty}^{\infty} \Gamma_{k-q, q, h}(E) e^{-iEt} dE, \\ \Gamma_{k-q, q, h}^1(t) &= \int_{-\infty}^{\infty} \Gamma_{k-q, q, h}^1(E) e^{-iEt} dE, \\ G_{k-q, h, q}(E) &= \int_{-\infty}^{\infty} G_{k-q, h, q}(E) e^{-iEt} dE; \end{aligned} \right\} \quad (8.10)$$

we find from the last three equations of the set (8.9)

$$\left. \begin{aligned} \Gamma_{k-q, q, h}(E) &= \frac{A_q (v_q + 1 - n_{k-q})}{E - T_{k-q} - \omega_q} G_k(E), \\ \Gamma_{k-q, q, h}^1(E) &= \frac{A_q (n_{k-q} + v_q)}{E - T_{k-q} + \omega_q} G_k(E), \\ G_{k-q, h, q}(E) &= \frac{A_q (n_{k-q} - n_k)}{E - T_k + T_{k-q}} G_q(E). \end{aligned} \right\} \quad (8.11)$$

The equations for  $G_k(E)$  and  $G_q(E)$  are then of the form

$$\left. \begin{aligned} \left\{ E - T_h - \sum_q A_q^2 \left[ \frac{\nu_q + 1 - n_{h-q}}{E - T_{h-q} - \omega_q} + \frac{n_{h-q} + \nu_q}{E - T_{h-q} + \omega_q} \right] \right\} G_h(E) = \frac{1}{2\pi}, \\ \left\{ E - \omega_q - \sum_{k, \sigma} A_q^2 \frac{n_{k-q} - n_k}{E - T_k + T_{k-q}} \right\} G_q(E) = \frac{1}{2\pi}. \end{aligned} \right\} \quad (8.12)$$

We introduce the functions  $M_k(E)$  and  $P_q(E)$  which by analogy with the quantum theory of fields can be called the mass and polarization operators

$$\left. \begin{aligned} M_h(E) &= \sum_q A_q^2 \left\{ \frac{\nu_q + 1 - n_{h-q}}{E - T_{h-q} - \omega_q} + \frac{n_{h-q} + \nu_q}{E - T_{h-q} + \omega_q} \right\}, \\ P_q(E) &= \sum_{k, \sigma} A_q^2 \frac{n_{k-q} - n_k}{E - T_k + T_{k-q}}. \end{aligned} \right\} \quad (8.13)$$

we have then

$$\left. \begin{aligned} G_h(E) &= \frac{1}{2\pi} \frac{1}{E - T_h - M_h(E)}, \\ G_q(E) &= \frac{1}{2\pi} \frac{1}{E - \omega_q - P_q(E)}. \end{aligned} \right\} \quad (8.14)$$

The fermion and boson single-particle Green functions can thus be expressed in terms of the mass and the polarization operator, respectively.

Using the Green functions we can also find the correlation functions

$$\left. \begin{aligned} \langle a_{h\sigma}(t') a_{h\sigma}(t) \rangle &= \int_{-\infty}^{\infty} J_h(\omega) e^{-i\omega(t-t')} d\omega, \\ \langle b_q(t') b_q(t) \rangle &= \int_{-\infty}^{\infty} J_q(\omega) e^{-i\omega(t-t')} d\omega, \end{aligned} \right\} \quad (8.15)$$

where  $J_k$  and  $J_q$  are in accordance with (3.25) defined by the relations

$$\left. \begin{aligned} G_h(\omega + i\varepsilon) - G_h(\omega - i\varepsilon) &= -iJ_h(\omega) (e^{\beta\omega} + 1), \\ G_q(\omega + i\varepsilon) - G_q(\omega - i\varepsilon) &= -iJ_q(\omega) (e^{\beta\omega} - 1). \end{aligned} \right\} \quad (8.16)$$

The fermion and boson distribution functions can be found by putting  $t = t'$  in Eqs. (8.15)

$$n_h = \int_{-\infty}^{\infty} J_h(\omega) d\omega; \quad \nu_q = \int_{-\infty}^{\infty} J_q(\omega) d\omega. \quad (8.17)$$

Using (8.14) and (8.13) to write Eqs. (8.16) down in detail, and using the symbolical identity (3.29) we get

$$M_h(\omega \pm i\varepsilon) = M_h(\omega) \mp i\gamma_h(\omega); \quad P_q(\omega \pm i\varepsilon) = P_q(\omega) \mp i\gamma_q(\omega) \quad (8.19)$$

( $\omega$  is real) where we have introduced the real functions

$$\left. \begin{aligned} M_h(\omega) &= P \sum_q A_q^2 \left\{ \frac{\nu_q + 1 - n_{h-q}}{\omega - T_{h-q} - \omega_q} + \frac{n_{h-q} + \nu_q}{\omega - T_{h-q} + \omega_q} \right\}, \\ P_q(\omega) &= P \sum_{k, \sigma} A_q^2 \frac{n_{k-q} - n_k}{\omega - T_k + T_{k-q}}, \end{aligned} \right\} \quad (8.20)$$

$$\gamma_h(\omega) = \pi \sum_l A_l^2 \left\{ (\nu_l + 1 - n_{h-l}) \delta(\omega - T_{h-l} - \omega_l) \right.$$

$$\left. + (n_{h-l} + \nu_l) \delta(\omega - T_{h-l} + \omega_l) \right\},$$

$$\gamma_q(\omega) = \pi \sum_{k, \sigma} A_q^2 (n_{k-q} - n_k) \delta(\omega - T_k + T_{k-q})$$

( $P$  indicates that the principal value of the corresponding integral must be taken).

The functions  $\gamma_k(\omega)$  and  $\gamma_q(\omega)$  which are also temperature dependent play the role of damping. As  $q \rightarrow 0$ , the damping  $\gamma_q \rightarrow 0$ .

It is clear from Eqs. (8.19) that the limiting values of the mass and polarization operators  $M_k(E)$  and  $P_q(E)$  when the complex argument  $E$  tends to the real axis from above and from below ( $\pm i\varepsilon \rightarrow 0$ ) are not the same, as  $\gamma_k(\omega)$  and  $\gamma_q(\omega)$  are finite quantities. The functions  $M_k(E)$  and  $P_q(E)$  have thus singularities on the real axis.

We get for the spectral intensities  $J_k(\omega)$  and  $J_q(\omega)$

$$\left. \begin{aligned} J_k(\omega) &= \frac{1}{\pi} \frac{\gamma_k(\omega) (e^{\beta\omega} + 1)^{-1}}{(\omega - T_k - M_k(\omega))^2 + \gamma_k^2(\omega)}, \\ J_q(\omega) &= \frac{1}{\pi} \frac{\gamma_q(\omega) (e^{\beta\omega} - 1)^{-1}}{(\omega - \omega_q - P_q(\omega))^2 + \gamma_q^2(\omega)}. \end{aligned} \right\} \quad (8.21)$$

(The expressions for  $M_k$ ,  $\gamma_k$ , and  $J_k$  were obtained in reference 19.) As  $\gamma_k$  and  $\gamma_q \rightarrow 0$  the spectral intensities (8.21) tend to a  $\delta$ -shape distribution.

For the electron and phonon distribution functions we get the equations

$$\left. \begin{aligned} n_h &= \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\gamma_h(\omega) (e^{\beta\omega} + 1)^{-1}}{(\omega - T_h - M_h(\omega))^2 + \gamma_h^2(\omega)} d\omega, \\ \nu_q &= \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\gamma_q(\omega) (e^{\beta\omega} - 1)^{-1}}{(\omega - \omega_q - P_q(\omega))^2 + \gamma_q^2(\omega)} d\omega. \end{aligned} \right\} \quad (8.22)$$

Equations (8.20) and (8.22) are a complete set of equations for the six functions  $M_k$ ,  $P_q$ ,  $\gamma_k$ ,  $\gamma_q$ ,  $n_k$ , and  $\nu_q$ .

We are thus led to a self-consistent set of nonlinear equations, which is very characteristic for approximations of the kind of interpolation decoupling methods for the chains of equations for Green functions.

In the limiting case when the damping may be considered to be very small, the functions (8.21) have a steep maximum at some value  $\omega = \tilde{\varepsilon}_k$  and  $\omega = \tilde{\omega}_q$ . Expanding the functions  $M_k(\omega)$  and  $P_q(\omega)$  in power series in  $\omega$  near these values and taking into account that  $\gamma_k(\omega)$  and  $\gamma_q(\omega)$  are slowly varying functions [ $\gamma_k(\omega) \cong \gamma_k(\tilde{\varepsilon}_k)$ ,  $\gamma_q(\omega) \cong \gamma_q(\tilde{\omega}_q)$ ] we get

$$\left. \begin{aligned} \frac{1}{\pi} \frac{\gamma_k(\omega)}{(\omega - T_h - M_h(\omega))^2 + \gamma_k^2(\omega)} &\cong \frac{1}{\pi} \frac{\left[ 1 - \left( \frac{dM_h}{d\omega} \right)_{\omega=\tilde{\varepsilon}_k} \right]^{-1} \tilde{\gamma}_k(\tilde{\varepsilon}_k)}{(\omega - \tilde{\varepsilon}_k)^2 + \tilde{\gamma}_k^2(\tilde{\varepsilon}_k)}, \\ \frac{1}{\pi} \frac{\gamma_q(\omega)}{(\omega - \omega_q - P_q(\omega))^2 + \gamma_q^2(\omega)} &\cong \frac{1}{\pi} \frac{\left[ 1 - \left( \frac{dP_q}{d\omega} \right)_{\omega=\tilde{\omega}_q} \right]^{-1} \tilde{\gamma}_q(\tilde{\omega}_q)}{(\omega - \tilde{\omega}_q)^2 + \tilde{\gamma}_q^2(\tilde{\omega}_q)}, \end{aligned} \right\} \quad (8.23)$$

where

$$\tilde{\gamma}_k = \gamma_k(\tilde{\varepsilon}_k) \left[ 1 - \left( \frac{dM_h}{d\omega} \right)_{\omega=\tilde{\varepsilon}_k} \right]^{-1};$$

$$\tilde{\gamma}_q = \gamma_q(\tilde{\omega}_q) \left[ 1 - \left( \frac{dP_q}{d\omega} \right)_{\omega=\tilde{\omega}_q} \right]^{-1};$$

$$\left( \frac{dM_h}{d\omega} \right)_{\omega=\tilde{\varepsilon}_k} \ll 1, \left( \frac{dP_q}{d\omega} \right)_{\omega=\tilde{\omega}_q} \ll 1$$

plays the role of damping and where  $\tilde{\epsilon}_k$  and  $\tilde{\omega}_q$  are determined from the transcendental equations

$$\tilde{\epsilon}_k - T_k - M_k(\tilde{\epsilon}_k) = 0; \quad \tilde{\omega}_q - \omega_q - P_q(\tilde{\omega}_q) = 0. \quad (8.24)$$

Replacing expressions (8.23) for very small values of the damping  $\tilde{\gamma}_k$  and  $\tilde{\gamma}_q$  by  $\delta$  functions, we shall have for them

$$\left[1 - \left(\frac{dM_k}{d\omega}\right)_{\omega=\tilde{\epsilon}_k}\right]^{-1} \delta(\omega - \tilde{\epsilon}_k), \quad \left[1 - \left(\frac{dP_q}{d\omega}\right)_{\omega=\tilde{\omega}_q}\right]^{-1} \delta(\omega - \tilde{\omega}_q)$$

[see (3.27)] and we get from Eqs. (8.22), dropping small terms, for the electron and phonon distribution functions

$$n_k = (e^{\beta\tilde{\epsilon}_k} + 1)^{-1}, \quad \nu_q = (e^{\beta\tilde{\omega}_q} - 1)^{-1}; \quad \left(\beta = \frac{1}{\theta}\right). \quad (8.25)$$

$\epsilon_k$  and  $\omega_q$  play thus the role of the elementary electron and phonon excitations.

It is clear from Eqs. (8.24) that the temperature dependent spectrum of the elementary excitations is determined by the real part of the mass operator for the electrons and of the polarization operator for the phonons.\*

We can use (8.20) to write the equations for the elementary excitations (8.24) in the form

$$\left. \begin{aligned} \tilde{\epsilon}_k &= T_k + P \sum_q A_q^2 \left\{ \frac{\nu_q + 1 - n_{k-q}}{\epsilon_k - T_{k-q} - \omega_q} + \frac{n_{k-q} + \nu_q}{\epsilon_k - T_{k-q} + \omega_q} \right\}, \\ \tilde{\omega}_q &= \omega_q + P \sum_{k,\sigma} A_q^2 \frac{n_{k-q} - n_k}{\omega_q - T_q + T_{k-q}} \end{aligned} \right\} \quad (8.26)$$

( $P$  indicates that one should take the principal value of the integral).

Equations (8.22) for  $n_k$  and  $\nu_q$  are Fermi-Dirac and Bose-Einstein distributions which are "smeared out" because of the interaction. The width of the smearing-out region is of the order of magnitude of the damping  $\tilde{\gamma}_k$  and  $\tilde{\gamma}_q$ . The damping is according to (8.19) determined by the imaginary part of the mass operator for the electrons or the polarization operator for the phonons.

In the example considered here we see thus that the concept of elementary excitations has an approximate meaning when one neglects damping.

The singularities of the Green functions (8.14) on the real axis of the energy [their existence follows from (8.16), since the spectral intensities (8.21) are not identically equal to zero] are not poles. This is clear from Eqs. (8.14) and (8.19) since  $\gamma_k$  and  $\gamma_q$  are not identically equal to zero, i.e., there is damping. The Green functions have thus a cut along the real axis. Only the approximate Green functions for which damping is neglected have poles on the real axis and they correspond to the energy (8.26) of the elementary excitations.

\*Similar relations for the Fröhlich Hamiltonian in the case of zero temperature were obtained in reference 47. See reference 18 for the case of a Hamiltonian with a direct interaction and non-vanishing temperature.

In the given approximation, which is based upon the decoupling of the functions (8.8), the higher-order Green functions  $\Gamma_{k-q, q, k}(E)$ ,  $\Gamma_{k-q, q, k}^1(E)$ , and  $G_{k-q, k, q}^1(E)$  have poles when  $E$  equals  $T_{k-q} + \omega_q$ ,  $T_{k-q} - \omega_q$ , and  $T_{k-q} - T_k$ , respectively. If we decouple not the Green functions (8.8), but Green functions of still higher order, the Fourier components of the Green functions (8.6) will no longer have poles and damping will occur for them as it does for the single-particle Green functions.

## 8.2. Electron-Lattice Interaction in Semiconductors

The usual methods of evaluating the electrical conductivity, starting from Bloch's transport equation, are valid only when one can speak about electron collisions, i.e., when the time of mean free path of the electrons  $\tau$  is appreciably larger than the uncertainty of the collisions time,<sup>58,55</sup> i.e.,  $\tau \gg h/kT$ . For semiconductors this criterion is satisfied very badly,<sup>58</sup> and the transport equation gives thus only a very rough estimate.

The quantum theory of the electrical conductivity without using Bloch's transport equation was recently considered by Kohn and Luttinger,<sup>60</sup> who solved the equations of motion of the complete density matrix, using perturbation theory and taking damping into account. Van Hove<sup>61</sup> was the first to consider equations for the density matrix, taking damping into account.

We shall give here briefly the method of evaluating the electrical conductivity of semiconductors using Green functions. For semiconductors one can, when the electron density is small, start from the picture of a single electron interacting with the phonon field. In that case one can also use the Hamiltonian (8.1), imposing the additional condition that the number of electrons  $N$  is equal to unity

$$N = \sum_{k\sigma} a_{k\sigma}^\dagger a_{k\sigma} = 1. \quad (8.27)$$

One must then take into account that for any operator the expressions

$$(a_{k_1\sigma_1}^\dagger \dots a_{k_s\sigma_s}^\dagger a_{q_1\sigma_1'} \dots a_{q_r\sigma_r'} B) = 0, \quad (8.28)$$

vanish when  $s > 1$  or  $r > 1$ , and this greatly simplifies the problem.

Since we consider only one electron, we cannot use a grand ensemble with a variable number of particles, but must use a canonical ensemble in which the number of particles is constant. In the present subsection we denote therefore by  $\langle \dots \rangle$  an average over a canonical ensemble.

We consider the interaction of the electron with the phonon field for the weak coupling case.

We introduce Green functions in which the operators  $A$  and  $B$  commute with the total number of particles ( $\eta = 1$ )

$$\left. \begin{aligned} G_{p_1 p_2; \sigma_2 \sigma_1}(t-t') &= \ll a_{p_1}^*(t) a_{p_2}(t); a_{\sigma_2}^*(t') a_{\sigma_1}(t') \gg, \\ G_{p_1 q p_2; \sigma_2 \sigma_1}(t-t') &= \ll a_{p_1}^*(t) b_q(t) a_{p_2}(t); a_{\sigma_2}^*(t') a_{\sigma_1}(t') \gg, \\ G_{p_1 q p_2; \sigma_2 \sigma_1}(t-t') &= \ll a_{p_1}(t) b_{-q}^*(t) a_{p_2}(t); a_{\sigma_2}^*(t') a_{\sigma_1}(t') \gg \end{aligned} \right\} \quad (8.29)$$

(we have dropped the spin indices) and we construct for them the chain of equations

$$\begin{aligned} i \frac{dG_{p_1 p_2; \sigma_2 \sigma_1}}{dt} &= \delta(t-t') \delta_{p_1 - \sigma_1} \delta_{p_2 - \sigma_2} (n_{p_1} - n_{p_2}) \\ &+ (T_{p_2} - T_{p_1}) G_{p_1 p_2; \sigma_2 \sigma_1} + \sum_{-p_2 - p_1 = q} A_q (G_{p_1 q p_2; \sigma_2 \sigma_1} + G_{p_1 q p_2; \sigma_2 \sigma_1}^i) \\ &- \sum_{p_1 - p_1 = q} A_q (G_{p_1 q p_2; \sigma_2 \sigma_1} + G_{p_1 q p_2; \sigma_2 \sigma_1}^i), \end{aligned} \quad (8.30a)$$

$$\begin{aligned} i \frac{dG_{p_1 q p_2; \sigma_2 \sigma_1}}{dt} &= \delta(t-t') \{ \delta_{p_2 - \sigma_2} \langle a_{p_1}^* b_q a_{\sigma_1} \rangle - \delta_{p_1 - \sigma_1} \langle a_{\sigma_2}^* b_q a_{p_2} \rangle \} \\ &+ (T_{p_2} - T_{p_1} + \omega_q) G_{p_1 q p_2; \sigma_2 \sigma_1} \\ &- \sum_{k_1 - p_1 = q_1} A_{q_1} \ll a_{k_1}^* (b_{q_1} + b_{-q_1}^*) b_q a_{p_2}; a_{\sigma_2}^*(t') a_{\sigma_1}(t') \gg \\ &+ \sum_{p_2 - k_1 = q_1} A_{q_1} \ll a_{p_1}^* b_q a_{k_1} (b_q + b_{-q}^*); a_{\sigma_2}^*(t') a_{\sigma_1}(t') \gg, \end{aligned} \quad (8.30b)$$

$$\begin{aligned} i \frac{dG_{p_1 q p_2; \sigma_2 \sigma_1}^i}{dt} &= \delta(t-t') \{ \delta_{p_2 - \sigma_2} \langle a_{p_1}^* b_{-q}^* a_{\sigma_1} \rangle - \delta_{p_1 - \sigma_1} \langle a_{\sigma_1}^* b_{-q}^* a_{p_2} \rangle \} \\ &+ (T_{p_2} - T_{p_1} - \omega_q) G_{p_1 q p_2; \sigma_2 \sigma_1}^i \\ &- \sum_{k_1 - p_1 = q_1} A_{q_1} \ll a_{k_1}^* (b_{q_1} + b_{-q_1}^*) b_{-q}^* a_{p_2}; a_{\sigma_2}^*(t') a_{\sigma_1}(t') \gg \\ &+ \sum_{p_2 - k_1 = q_1} A_{q_1} \ll a_{p_1}^* b_{-q}^* (b_{q_1} + b_{-q_1}^*) a_{k_1}; a_{\sigma_2}^*(t') a_{\sigma_1}(t') \gg. \end{aligned} \quad (8.30c)$$

In the case of a low electron density one can neglect the reaction of the electrons on the lattice and assume that the average occupation number of the lattice phonons

$$v_q = \langle b_q^* b_q \rangle = (1 - e^{\beta \omega_q})^{-1} \quad \left( \beta = \frac{1}{\theta} \right)$$

is the same as if there were no electrons. We decouple then the Green functions by pairing off the operators  $b_q$  referring to the same time

$$\left. \begin{aligned} \ll a_{p_1}^* (b_{q_1} + b_{-q_1}^*) b_q a_{p_2}; a_{\sigma_2}^*(t') a_{\sigma_1}(t') \gg &= v_q G_{p_1 p_2; \sigma_2 \sigma_1} \delta_{q+q_1}, \\ \ll a_{p_1}^* b_q (b_{q_1} + b_{-q_1}^*) a_{p_2}; a_{\sigma_2}^*(t') a_{\sigma_1}(t') \gg &= (1 + v_q) G_{p_1 p_2; \sigma_2 \sigma_1} \delta_{q+q_1} \end{aligned} \right\} \quad (8.31)$$

Equations (8.30b) and (8.30c) are then of the form

$$\begin{aligned} (E + T_{p_1} - T_{p_2} - \omega_q) G_{p_1 q p_2; \sigma_2 \sigma_1}(E) &= \frac{1}{2\pi} \{ \langle a_{p_1}^* b_q a_{\sigma_2} \rangle \delta_{p_2 - \sigma_2} - \langle a_{\sigma_2}^* b_q a_{p_2} \rangle \delta_{\sigma_1 - p_1} \} \\ &+ A_q \{ (1 + v_q) G_{p_1 p_2 + q; \sigma_2 \sigma_1}(E) - v_q G_{p_1 - q, p_2; \sigma_2 \sigma_1}(E) \}, \\ (E + T_{p_1} - T_{p_2} + \omega_q) G_{p_1 q p_2; \sigma_2 \sigma_1}^i(E) &= \frac{1}{2\pi} \{ \langle a_{p_1}^* b_{-q}^* a_{\sigma_2} \rangle \delta_{p_2 - \sigma_2} \\ &- \langle a_{\sigma_2}^* b_{-q}^* a_{p_2} \rangle \delta_{\sigma_1 - p_1} \} + A_q \{ v_q G_{p_1 p_2 + q; \sigma_2 \sigma_1}(E) \\ &- (1 + v_q) G_{p_1 - q, p_2; \sigma_2 \sigma_1}(E) \}, \end{aligned} \quad (8.32)$$

where we have changed to Fourier components. We can easily evaluate the average values of products of three

operators such as  $\langle a_p^* b_q a_g \rangle$ , if we take into consideration that

$$\frac{d}{dt} \langle a_p^*(t) b_q(t) a_g(t) \rangle = 0,$$

and write this relation down explicitly using the equations of motion (8.3) in the same approximation as used for (8.31), and using (8.28). We get then

$$\left. \begin{aligned} \langle a_{p_1}^* b_q a_{\sigma_1} \rangle &= \frac{A_q \{ v_q n_{q_1} - (v_q + 1) n_{p_1} \}}{T_{q_1} - T_{p_1} + \omega_q} \delta_{p_1 - \sigma_1 - q}, \\ \langle a_{p_1}^* b_{-q}^* a_{\sigma_1} \rangle &= \frac{A_q \{ (1 + v_q) n_{q_1} - v_q n_{p_1} \}}{T_{q_1} - T_{p_1} - \omega_q} \delta_{p_1 - \sigma_1 - q}. \end{aligned} \right\} \quad (8.33)$$

These expressions contain besides  $A_q$ , which is supposed to be small, also a factor  $n_p$ . In our case of low electron density these terms will thus be small, so that we can to a first approximation neglect in Eqs. (8.32) the first two terms. Changing in Eq. (8.30a) to Fourier components and substituting into it Eqs. (8.32), after neglecting these terms, we get an integral equation for the function  $G_{p_1 p_2; \sigma_2 \sigma_1}(E)$

$$\begin{aligned} (E + T_{p_1} - T_{p_2}) G_{p_1 p_2; \sigma_2 \sigma_1}(E) &+ \sum_q A_q^2 \left\{ \frac{1 + v_q}{E + T_{p_1} - T_{p_2 + q} - \omega_q} \right. \\ &+ \frac{v_q}{E + T_{p_1} - T_{p_2 - q} + \omega_q} + \frac{v_q}{E + T_{p_1 + q} - T_{p_2} - \omega_q} \\ &+ \left. \frac{1 + v_q}{E + T_{p_1 + q} - T_{p_2} + \omega_q} \right\} G_{p_1 p_2; \sigma_2 \sigma_1} - \sum_q A_q^2 \left\{ \frac{v_q}{E + T_{p_1} - T_{p_2 + q} - \omega_q} \right. \\ &+ \frac{1 + v_q}{E + T_{p_1} - T_{p_2 + q} + \omega_q} + \frac{1 + v_q}{E + T_{p_1 + q} - T_{p_2} - \omega_q} \\ &+ \left. \frac{v_q}{E + T_{p_1 + q} - T_{p_2} + \omega_q} \right\} G_{p_1 + q, p_2 + q; \sigma_2 \sigma_1} \\ &= \frac{1}{2\pi} (n_{p_1} - n_{p_2}) \delta_{p_2 - \sigma_2} \delta_{p_1 - \sigma_1}. \end{aligned} \quad (8.34)$$

One can also easily take into account the terms (8.33) which lead in the right hand side of Eq. (8.34) to an additional term with an inhomogeneity of higher order than the term written down.

Equation (8.34) has the form of a transport equation\* as  $E \rightarrow \pm i\epsilon \rightarrow 0$ , as one can easily verify by using (3.29) to transform the integrand; terms corresponding to principal-value integrals cancel one another then, and there remain terms with  $\delta$  functions, expressing the fact that energy is conserved during collisions.

Assuming that a solution of equations of the kind of (8.34) is known one can evaluate from (4.26) the electrical conductivity tensor. It is important to note that we have here not used a transport equation which might in the present case not be applicable.

## 9. CONCLUSIONS

1. Double-time Green functions (retarded and advanced) are a convenient means to study systems of

\*The connection between the equation for the pair distribution function and the transport equation is also true for an imperfect Fermi-gas.<sup>14</sup>

large numbers of interacting particles; this is connected with the fact that one can continue them analytically in the complex plane. The Green functions are analytical in the whole of the complex energy plane, but they have, generally speaking, a cut on the real axis (Sec. 3).

2. The Green functions satisfy a set of coupled equations in which only double-time functions occur (Sec. 2). Spectral theorems (Sec. 3) enable us to formulate boundary conditions for these equations. If one decouples these equations by some kind of approximation (see, for instance, Secs. 6 to 8) one is able to obtain a complete set of equations for the Green functions, and solving these one can evaluate the thermodynamic functions of the system.

3. Green functions are also convenient in studying the kinetics of weakly-non-equilibrium processes. The transport coefficients can be expressed in terms of the Fourier components of the retarded Green functions evaluated for the state of statistical equilibrium (Sec. 4).

4. The examples considered here can be divided into three groups: perfect systems (Sec. 5), model systems with interactions (Sec. 6), and real systems with interactions (Secs. 7 and 8).

For perfect systems (the perfect Fermi-Dirac or Bose-Einstein gas) the Green functions have poles on the real axis. The spectrum of the elementary excitations is the same as the poles of the single-particle Green function, there is no damping, and the time correlation functions oscillate as  $|t' - t| \rightarrow \infty$ . If one assumes that there is an infinitesimal interaction in the perfect gas (which is necessary in order that statistical equilibrium can be established in it) we can assume that the perfect gas possesses infinitesimally small damping.

For model systems with interaction (Sec. 6) the Green functions have poles on the real axis. The (temperature dependent) elementary excitation spectrum is the same as the poles of the single-particle Green function. There is no damping (more exact: it is asymptotically small as  $V \rightarrow \infty$ ,  $V/N = \text{const.}$ ). The time correlation functions oscillate as  $|t' - t| \rightarrow \infty$  with an asymptotically small damping.

For real systems with interaction the Green functions have a cut along the real axis and have poles only in first approximation. The damping is finite. If one neglects damping, the approximate Green functions have poles which can be identified with the (temperature dependent) energy of the elementary excitations. The energy of the elementary excitations has therefore a well-defined meaning only when damping is neglected. The time correlation functions oscillate as  $|t' - t| \rightarrow \infty$  with a finite damping. The properties enumerated here are given in the table.

One must expect that the properties of Green functions illustrated by us with examples will also occur for other systems which are studied in statistical mechanics.

Properties of Statistical Systems

	Perfect systems	Model systems	Real Systems
Singularities of the Green functions	Analytical in the upper and lower energy half plane Poles on the real energy axis	Poles on the real energy axis	A cut along the real energy axis
Elementary excitation spectrum	The same as the poles of the single-particle Green function	The same as the poles of the single-particle Green function; generally speaking temperature dependent	To a first approximation, the same as the poles of the Green function. In higher orders there are no poles; the spectrum is defined in as far as damping can be neglected.
Damping	No damping	No damping (more exactly: asymptotically small damping)	Finite damping
Behavior of the time correlation functions as $ t' - t  \rightarrow \infty$	Oscillate	Oscillate with asymptotically small damping	Oscillate with finite damping

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#### Translator's Comments:

This paper should be compared with the series of papers by Martin and Schwinger, of which only the first part has appeared so far.<sup>1</sup> Zubarev does not go into as detailed a discussion of the mathematical properties of Green functions, concentrating rather

on applications. It is surprising that neither Zubarev nor Martin and Schwinger refer to the early papers by Husimi<sup>2</sup> and Koppe,<sup>3</sup> who noted the connection between the density matrix and Green functions, or to Salam's paper<sup>4</sup> where, probably for the first time, Green function techniques were applied to solid-state many-body problems (in this case, superconductivity). Zubarev's paper discusses double-time generalized Green functions which are the averages of the time-ordered products of any two operators rather than the normally used multiple-time many-particle Green functions of field theory which are the averages of the time-ordered products of any number of second-quantized wave-functions. It must be mentioned, however, that Martin and Schwinger in fact used the double-time Green functions in all applications, and that in most applications Zubarev's Green functions are, indeed, the many-particle ones, although Zubarev makes it clear that the generalized Green functions can often be used to advantage, for instance in the theory of ferromagnetism.

Zubarev stresses the advantage of the advanced and retarded Green functions rather than the causal ones normally used, for in-

stance by Martin and Schwinger. The advantage lies in the fact that the advanced and retarded Green functions, or rather their Fourier transforms, can be analytically continued in the complex energy plane.

The literature quoted by Zubarev is much more comprehensive than that quoted by Martin and Schwinger and covers both Russian and non-Russian references. Recent developments, especially in solid state theory, have largely occurred in the Soviet Union, apart from those on linked cluster expansions of the grand partition function. These expansions – where the Green functions occur as propagators – are discussed neither by Zubarev nor by Martin and Schwinger.

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Translated by D. ter Haar