DIAGRAM TECHNIQUE FOR NONEQUILIBRIUM PROCESSES

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A graph technique analogous to the usual Feynman technique in field theory is developed for calculating Green's functions for particles in a statistical system which under the action of an external field deviates to any arbitrary extent from the state of thermodynamic equilibrium. It is found that in order to describe such a system it is necessary to introduce two Green's functions for each type of particles. The equation for one of these functions is a generalization of the usual Boltzmann kinetic equation.

THE use of quantum field theory methods has turned out to be very effective for the formulation and for the solution of problems in statistical physics. A number of prescriptions has been given for the description of thermodynamic characteristics of equilibrium systems[1-6] and of the ground state of a many-body system[7-9]. In the papers of Konstantinov and Perel'[10], Dzyaloshinskiĭ[11] and Mills[12] a technique has been developed for the calculation of time dependent quantities (kinetic coefficients) in systems in thermodynamic equilibrium. In carrying out this program the deviation of the system from the Gibbs equilibrium distribution was assumed to be small, i.e., the external field was taken to be sufficiently small. The present paper is devoted to the application of analogous methods to the description of essentially nonequilibrium systems, for example, such systems as the system of electrons in a strong electric field. In the simplest cases in order to describe such systems Boltzmann's kinetic equation or the system of coupled equations proposed by Bogolyubov[13] are used.

We shall obtain below a system of equations for the Green's functions of the particles in the system, and we shall show that one of these equations is essentially analogous to the kinetic equation. The appearance of such an equation—an additional one in comparison with systems in thermodynamic equilibrium—in the problem under consideration is quite natural, since we must have an equation which describes the distribution of particles in the system. In the equilibrium case this is given by the Gibbs canonical distribution. Our diagram technique will be close to Mills' technique for equilibrium systems. This technique has the advantage that it is completely analogous to the usual Feynman technique in field theory, with the only differ-

ence that the number of Green's functions appearing in it is increased. In the course of the discussion there appears automatically a function which describes the distribution of the particles in the system, and the equation for this function plays the role of the kinetic equation.

Following the method of Konstantinov and Perel' we shall define the density matrix ρ for the system by the usual equation

$$i\partial\rho / \partial t = [H_i, \rho]_- \equiv H_i(t)\rho(t) - \rho(t)H_i(t) \qquad (1)$$

with the boundary condition

$$\rho(t = -\infty) = \rho_0 = \exp\{\Psi_0 - H_0(-\infty)) / kT\}, \quad (2)$$

where $H = H_0 + H_i$ is the Hamiltonian of the system

$$H_0(t) = \int \psi_0{}^+(\mathbf{r}t) \left\{\varepsilon\left(-i\hbar\nabla - \frac{e}{c}\mathbf{A}\right) + e\Phi\right\}$$

$$\times \psi_0(\mathbf{r}t)\, d\mathbf{r} + H_T. \qquad (3)$$

The first term in H_0 is the energy of noninteracting electrons in an external electromagnetic field $\{\mathbf{A}(\mathbf{r}t), \Phi(\mathbf{r}t)\}$, the second is the Hamiltonian of the heat bath in contact with the system under consideration, $\epsilon(\mathbf{p})$ is the dispersion law for the electrons, Ψ_0 is the initial free energy.

The field operators ψ_0 and ψ_0^+ are defined in the following manner: let $\varphi_{\mathbf{p}}(\mathbf{r}t)$ be the complete system of functions determined by the equation

$$\left\{\varepsilon\left(-i\nabla - \frac{e}{c}\mathbf{A}(\mathbf{r}t)\right) + e\Phi(\mathbf{r}t) - i\frac{\partial}{\partial t}\right\}\varphi_{\mathbf{p}}(\mathbf{r}t) = 0 \quad (4)$$

and by the boundary condition at $t \to -\infty$

$$\varphi_{\mathbf{p}}(\mathbf{r}t) \to \exp\{i(\mathbf{p}\mathbf{r} - \varepsilon_{\mathbf{p}}t)\}, \qquad (5)$$

where we consider the external field to be switched off at $t \to -\infty$, i.e., $(\mathbf{A}, \Phi) \to 0$. Then the field operator $\psi_0(\mathbf{r}t)$ is defined by the relation

$$\psi_0(\mathbf{r}t) = \sum_\mathbf{p} a_\mathbf{p}\varphi_\mathbf{p}(\mathbf{r}t), \qquad (6)$$

where $a_\mathbf{p}$ are the usual Fermi operators which satisfy the commutation relations

$$[a_\mathbf{p}^+ a_{\mathbf{p}'}]_+ \equiv a_\mathbf{p}^+ a_{\mathbf{p}'} + a_{\mathbf{p}'} a_\mathbf{p}^+ = \delta_{\mathbf{p}\mathbf{p}'}. \qquad (7)$$

Utilizing the fact that the functions $\varphi_\mathbf{p}(\mathbf{r}t)$ form at any arbitrary instant of time a complete orthogonal system, and formulas (6) and (7), it can be easily shown that for coincident times

$$[\psi_0^+(\mathbf{r}t), \psi_0(\mathbf{r}'t)]_+ = \delta(\mathbf{r} - \mathbf{r}') \qquad (8)$$

and in virtue of this the operators $\psi_0(\mathbf{r}t)$ satisfy the free equations of motion

$$i\partial\psi_0/\partial t = [\psi_0, H_0]_-, \qquad (9)$$

i.e., we have from the outset defined the field operators in the interaction representation.

We note that the operator $H_0(t)$ differs in the Schrödinger representation and in the interaction representation in contrast to the usual case, when all the external fields are independent of the time. Having in mind such a definition of the field operators we have from the outset written equation (1) in the interaction representation leaving in it only the operator for the interaction energy H_i which, for the sake of definiteness, we shall in future write in the form

$$H_i(t) = g \int \psi_0^+(\mathbf{r}t)\psi_0(\mathbf{r}t)\varphi_0(\mathbf{r}t)\,d\mathbf{r}, \qquad (10)$$

where g is a dimensionless coupling constant. Such an expression describes the interaction between electrons and phonons in solids, and also can be utilized to describe the Coulomb interaction of charged particles if we write a separate equation for the Coulomb field.

Equation (1) for the density matrix $\rho(t)$ can be formally solved with the aid of the S-matrix

$$S(t, -\infty) = T \exp\left\{-\frac{i}{\hbar}\int_{-\infty}^{t} H_i(\tau)\,d\tau\right\}, \qquad (11)$$

which satisfies the equation

$$i\partial S/\partial t = H_i(t)S(t). \qquad (12)$$

The symbol T in (11) denotes a time-ordered product defined in the usual manner. Then we have

$$\rho(t) = S(t, -\infty)\rho_0 S^+(t, -\infty)$$

$$= S(t, -\infty)\rho_0 S(-\infty, t). \qquad (13)$$

The density matrix defined in this manner depends explicitly on the time. The average value of an arbitrary operator $L_0(t)$ at time t has the form

$$\langle L_0(t)\rangle = \mathrm{Tr}\{\rho(t)L_0(t)\}, \qquad (14)$$

where the subscript zero on the operator L_0 shows that this operator is taken in the interaction representation, i.e., its time dependence is determined by the free equation of motion in the external field

$$i\partial L_0/\partial t = [L_0(t), H_0(t)]_-, \qquad (15)$$

since the density matrix $\rho(t)$ itself was defined by us in the interaction representation. In future, however, we shall have occasion to deal with correlation functions of several field operators taken at different instants of time. In these cases it will be more convenient for us to transfer the entire time dependence to these operators, and to regard the density matrix as being independent of the time, i.e., to go over to the Heisenberg representation. In this case the field operators satisfy the complete equations of motion

$$i\partial\psi/\partial t = [\psi, H]_-. \qquad (16)$$

For the time-independent density matrix we can take the value of the matrix determined by expression (13) at a certain fixed instant of time, for example, t = 0, having thus included in it all the changes which the distribution ρ_0 (2) had undergone when the external field and the interaction in the system were switched on. In order to convince ourselves that such a procedure is correct we shall, for example, show that in the case of a system in thermodynamic equilibrium it leads to the Gibbs canonical distribution, as it ought. In order to do this we utilize the well-known relation[14,15]

$$S(0, -\infty)H_0 S^+(0, -\infty)$$

$$= H - i\delta g\frac{dS(0, -\infty)}{dg}S^+(0, -\infty), \qquad (17)$$

where δ is a parameter describing the adiabatic switching-on of the interaction, i.e., the interaction constant g in (10) is considered to be time dependent, in accordance with $g(t) = ge^{\delta t}$. After going to the limit $\delta \to 0$ the second term in (17) turns into a c-number equal to the sum of all the vacuum loops and describing the correction to the free energy of the system[1-3]. Therefore, for the given case of an equilibrium system

$$\rho = \rho(0) = S(0, -\infty)\rho_0 S^+(0, -\infty) = e^{(\Psi - H)/kT}, \quad (18)$$

where H is the total Hamiltonian, while Ψ is the total free energy.

Having defined the density matrix as $\rho(0)$ we must utilize such Heisenberg field operators $\psi(\mathbf{r}, t)$, which at t = 0 go over into the free $\psi_0(\mathbf{r}t)$. In other words,

$$\psi(\mathbf{r}t) = S(0, t)\psi_0(\mathbf{r}i)S(t, 0), \qquad (19)$$

where, by definition,

$$S(t', t) = T \exp\left\{-i\int_t^{t'} H_i(\tau)d\tau\right\} \qquad (20)$$

$$= S(t', -\infty)S^+(t, -\infty).$$

Utilizing these relations and the definition of the Heisenberg density matrix ρ, the average value of the T-product of arbitrary Heisenberg operators $L(t)$, $M(t')$ ... can be brought to the form

$$\langle TL(t)M(t')...\rangle = \mathrm{Tr}\{\rho TL(t)M(t')...\}$$

$$= \mathrm{Tr}\{S(0, -\infty)\rho_0 S(-\infty, 0)TL(t)M(t')...\}$$

or, commuting in the argument of Tr the operator $S(0, -\infty)$ and going over to operators in the interaction representation,

$$\langle TL(t)M(t')...\rangle$$

$$= \mathrm{Tr}\{\rho_0 S(-\infty, 0)[TS(0, t)L_0(t)S(t, t')M_0(t')...]$$

$$\times S(0, -\infty)\} = \mathrm{Tr}\{\rho_0 T_c[S_c L_0(t)M(t')...]\}, \qquad (21)$$

where T_c indicates ordering along the contour c, going from $-\infty$, passing the points t, t' ... and then returning back to $-\infty$; S_c is the complete S-matrix defined along the whole contour c. Ordering along c means that the points on the return branch of this contour correspond to later times than the points on the original direct branch, and of any two points on the return path the later one is that which is closer to $-\infty$.

However, evaluation of integrals along the contour c is inconvenient. Therefore, we perform in (21) the following identity transformation: we insert in the argument of T_c the factor $S(t_0, +\infty)\times S(+\infty, t_0)$ which is identically equal to unity, taking the point t_0 to lie on the contour c later than that one of the points t, t' ... which lies on the extreme right. This is equivalent to cutting the contour C. to the right of the point lying on the extreme right and inserting into it a piece which goes to $+\infty$ and returns. The resultant contour C traverses the whole time axis from $-\infty$ to $+\infty$ and then back again from $+\infty$ to $-\infty$. Formula (21) is thus brought to the final form

$$\langle TL(t)M(t')...\rangle = \mathrm{Tr}\{\rho_0 T_C(S_C L_0(t)M_0(t')...]\}, \qquad (22)$$

with all the arguments t, t' ... considered as lying on the positive $(-\infty, +\infty)$ branch of the contour C.

But use of the contour C enables us to write in the form of a T-product also the usual correlation function of two operators $L(t)$ and $M(t')$. Indeed, we shall assign to points lying on the positive (pro-

ceeding from $-\infty$ to $+\infty$) branch of the contour the subscript $+$, and to points lying on the negative branch the subscript $-$. Then evidently we have

$$\langle L(t)M(t')\rangle = \mathrm{Tr}\{\rho_0 T_C[S_C L_0(t_-)M_0(t_+')]\}, \qquad (23)$$

since in accordance with the definition of the T_C-product the point t_+' always precedes the point t_-. This possibility leads to the fact that the diagram technique obtained below enables us to evaluate directly not only the Green's functions for the particles, but also the usual average values of operators.

The averages of T-products of the type (22) and (23) can be decomposed in the usual manner[2] into a sum of Feynman graphs evaluated in accordance with the following rules.

1. An n-th order graph contains 2n points along the real time axis. Moreover, each point can lie either on the positive or on the negative branch of the contour C, and this is denoted respectively by the subscripts $+$ or $-$. An integration with respect to the coordinates of all the internal points is carried out over the whole volume and over time from $-\infty$ to $+\infty$. Each internal point is put in correspondence with a factor g, if its subscript is $+$, and with the factor $-g$, if its subscript is $-$.

2. One phonon and two electron lines emerge from (or enter) each point. Each of these lines is set in correspondence with one of four functions depending on the signs of the points which this line joins:

a) if the line goes from the point $-$ to the point $+$, it is set in correspondence with the function

$$G_0^+(\mathbf{r}t_+, \mathbf{r}'t_-') = -i\mathrm{Tr}\{\rho_0 T_C[\psi_0(\mathbf{r}t_+), \psi_0^+(\mathbf{r}'t_-')]\}$$

$$= i\langle\psi_0^+(\mathbf{r}'t_+')\psi_0(\mathbf{r}t_-)\rangle_0. \qquad (24)$$

the symbol $\langle...\rangle_0$ denotes averaging using the matrix ρ_0;

b) if the line goes from the point $+$ to the point $-$, it is set in correspondence with the function

$$G_0^-(\mathbf{r}t_-, \mathbf{r}'t_+') = -i\mathrm{Tr}\{\rho_0 T_C[\psi_0(\mathbf{r}t_-)\psi_0^+(\mathbf{r}'t_+')]\}$$

$$= -i\langle\psi_0(\mathbf{r}t_-)\psi_0^+(\mathbf{r}'t_+')\rangle_0; \qquad (25)$$

c) if the line goes from the point $+$ to the point $+$, then it is set in correspondence with the usual causal Green's function

$$G_0^c(\mathbf{r}t_+, \mathbf{r}'t_+') = -i\mathrm{Tr}\{\rho_0 T_C[\psi_0(\mathbf{r}t_+)\psi_0^+(\mathbf{r}'t_+')]\}$$

$$= -i\langle T\psi_0(\mathbf{r}t_+)\psi_0^+(\mathbf{r}'t_+')\rangle_0; \qquad (26)$$

d) and, finally, the line connecting the point $-$ with the point $-$ is set in correspondence with the function

$$\widetilde{G}_0{}^c(\mathbf{r}t_-, \ \mathbf{r}'t_-') = -i\mathrm{Tr}\{\rho_0 T_C[\psi_0(\mathbf{r}t_-)\psi_0{}^+(\mathbf{r}'t_-')]\}$$

$$= -i\langle \widetilde{T}\psi_0(\mathbf{r}t_-)\psi_0{}^+(\mathbf{r}'t_-')\rangle_0. \quad (27)$$

In the last formula $\widetilde{T}$ denotes the product ordered with respect to the reversed time, i.e.,

$$\widetilde{T}\psi_0(t)\psi_0{}^+(t') = \begin{cases} \psi_0(t)\psi_0{}^+(t'), & \text{if } t < t', \\ -\psi_0{}^+(t')\psi_0(t), & \text{if } t > t'. \end{cases}$$

We shall henceforth omit everywhere the indices + and − in the time arguments of the Green's functions, since the index ascribed to the Green's function itself uniquely determines the positions of its final and initial points on the branches of the contour C. The functions $G_0{}^c$ and $\widetilde{G}_0{}^c$ are related to $G_0{}^\pm$ by the obvious relations

$$G_0{}^c(\mathbf{r}t, \ \mathbf{r}'t') = \theta(t - t')G_0{}^-(\mathbf{r}t, \ \mathbf{r}'t')$$
$$+ \theta(t' - t)G_0{}^+(\mathbf{r}t, \ \mathbf{r}'t'), \quad (28)$$

$$\widetilde{G}_0{}^c(\mathbf{r}t, \ \mathbf{r}'t') = \theta(t - t')G_0{}^+(\mathbf{r}t, \ \mathbf{r}'t')$$
$$+ \theta(t' - t)G_0{}^-(\mathbf{r}t, \ \mathbf{r}'t'); \quad (29)$$

$$\theta(x) = \tfrac{1}{2}(1 + \mathrm{sign}\ x).$$

The Green's functions for Bose particles are defined in an analogous manner.

The further rules for calculation are completely analogous to the usual Feynman rules, and, therefore, we shall not state them in detail. We only note that a diagram with 2n points contains the factor i^{n+2F}, where F is the number of closed loops in it, and that the unconnected diagrams must be omitted since they cancel with the trace of the density matrix which we have for this reason omitted in advance in the denominators of all the formulas (21)−(29).

It should also be noted that the applicability of Wick's theorem to the expansion of the T-products (22), (23) is not entirely obvious. Strictly speaking, when four or more field operators having the same momentum are averaged over the distribution ρ_0, the T-product does not decompose into a sum of products of T-products taken a pair at a time. But for systems of Fermi-particles and of phonons (phonons correspond to a real field) considered by us Wick's theorem is completely rigorous. In other cases the contribution of two or more pairs of operators whose momenta are the same is generally of order 1/N, where N is the number of degrees of freedom, since integration is carried out over all the internal momenta. An exception can occur in the case of systems in which phenomena of the type of Bose-condensation are observed. The technique under consideration is not directly applicable to these systems.

We now define the complete Green's functions:

$$G^c(\mathbf{r}t, \ \mathbf{r}'t') = -i\mathrm{Tr}\{\rho_0 T_C[\psi_0(\mathbf{r}t_+)\psi_0{}^+(\mathbf{r}'t_+')S_C]\}, \quad (30)$$

$$\bar{G}^c(\mathbf{r}t, \ \mathbf{r}'t') = -i\mathrm{Tr}\{\rho_0 T_C[\psi_0(\mathbf{r}t_-)\psi_0{}^+(\mathbf{r}'t_-')S_C]\}, \quad (31)$$

$$G^\pm(\mathbf{r}t, \ \mathbf{r}'t') = -i\mathrm{Tr}\{\rho_0 T_C[\psi_0(\mathbf{r}t_\pm)\psi_0{}^+(\mathbf{r}'t_\mp')S_C]\}, \quad (32)$$

which are sums of all the connected diagrams with one entering and one emerging line which differ from one another by the location of the initial and the final points on different branches of the contour C. The following relations involving them are preserved

$$G^c(\mathbf{r}t, \ \mathbf{r}'t') = \theta(t - t')G^-(\mathbf{r}t, \ \mathbf{r}'t') + \theta(t' - t)G^+(\mathbf{r}t, \ \mathbf{r}'t'), \quad (33)$$

$$\widetilde{G}^c(\mathbf{r}t, \ \mathbf{r}'t') = \theta(t - t')G^+(\mathbf{r}t, \ \mathbf{r}'t') + \theta(t' - t)G^-(\mathbf{r}t, \ \mathbf{r}'t'), \quad (34)$$

i.e., only the two functions G^+ and G^- are independent, and even they are related by the obvious expression

$$\lim_{t' \to t} \{G^+(\mathbf{r}t, \ \mathbf{r}'t') - G^-(\mathbf{r}t, \ \mathbf{r}'t')\} = -i\delta(\mathbf{r} - \mathbf{r}'). \quad (35)$$

The subsequent technique of calculating the various quantities and the form of the equations are both considerably simplified if, following Mills[12], we go over to the matrix form of writing the equations. We define a two-rowed matrix G in the following manner:

$$G = \begin{pmatrix} G^c & G^- \\ G^+ & \widetilde{G}^c \end{pmatrix}. \quad (36)$$

Then, as can be easily seen, summation over the subscript ± at each point reduces to matrix multiplication of matrices corresponding to lines emerging from that point. But since there are three such lines—two electron lines and one phonon line—it is necessary to connect them by means of a vertex matrix of the third rank

$$\gamma_{ij}{}^k = \delta_{ij}(\sigma_z)_{jk}, \quad (37)$$

where the subscripts refer to the electron lines, and the superscript to the phonon line; σ_z is the third Pauli matrix; the fact that for k = 2 it is negative takes into account the factor −1 for points on the return branch of the contour C (in matrix notation the points + correspond to subscripts 1, and the points − correspond to subscripts 2).

An arbitrary matrix element can now be written in the form of a product of blocks of the type

$$G_{li}\gamma_{ij}{}^k G_{jm}D_{kn},$$

in which summation is assumed to be carried out over repeated subscripts. D is the matrix for the Green's functions for Bose-particles defined in

analogy with (36). With this notation we no longer need to distinguish the points denoted by + and −. The technique for the evaluation of any arbitrary graph now becomes a purely Feynman one with the only difference that to each line we now set in correspondence the matrix (36), and to each point the vertex matrix (37).

Summation of the diagrams for the complete Green's function leads to an equation of the type of Dyson's equation:

$$G(\mathbf{r}t, \mathbf{r}'t') = G_0(\mathbf{r}t, \mathbf{r}'t')$$

$$+ ig^2 \int G_0(\mathbf{r}t, \mathbf{r}_1t_1) \Sigma(\mathbf{r}_1t_1, \mathbf{r}_2t_2) G(\mathbf{r}_2t_2, \mathbf{r}'t') \, d\mathbf{r}_1 d\mathbf{r}_2 dt_1 dt_2.$$

$$(38)$$

The self energy matrix Σ is defined by relation (39) in which the complete vertex matrix $\Gamma_{ij}^k(x, x'; y)$ is the sum of all the irreducible diagrams with one incoming (at the point x) and one outgoing (at the point x') electron line and one external phonon line at the point y:

$$\Sigma_{ij}(x, x')$$

$$= \int \gamma_{ii'}{}^h G_{i'j'}(x, x_1) \Gamma_{j'j}{}^{h'}(x_1, x' \ y) D_{h'h}(y, x) d^4x_1 d^4y,$$

$$x = (\mathbf{r}, t). \qquad (39)$$

Dyson's equation in integral form (38) appears to be unsatisfactory since it contains the function G_0 which explicitly depends on the initial distribution ρ_0. At the same time from physical considerations it follows that if the system is in contact with a heat bath, then after sufficient time has elapsed it must reach a state which is, generally speaking, not stationary, since the external field depends on the time, but which is independent of the initial conditions. This inconsistency can be easily avoided by going over to the differential form of Dyson's equation, i.e., by multiplying (38) by the operator matrix

$$\hat{G}_0^{-1} = G_0^{-1}(x)\sigma_z, \qquad (40)$$

where the differential operator G_0^{-1} is defined by

$$G_0^{-1}(x) = i\frac{\partial}{\partial t} - \varepsilon\left(-i\nabla - \frac{e}{c}\mathbf{A}(x)\right) - e\Phi(x), \quad (41)$$

$x = (\mathbf{r}t)$. Then Eq. (38) is reduced to the form

$$\hat{G}_0^{-1}(x)G(x, x')$$

$$= ig^2 \int \Sigma(x, x_1) G(x_1, x') dx_1 + \delta(x - x'). \qquad (42)$$

In deriving this formula we have utilized the obvious relations

$$G_0^{-1}(x)G_0^{\pm}(x, x') = 0, \qquad G_0^{-1}(x)G_0^c(x, x') = \delta(x - x'),$$

$$G_0^{-1}(x)\tilde{G}_0^c(x, x') = -\delta(x - x').$$

Equation (42) contains only complete Green's functions which do not explicitly depend on ρ_0. At the same time its solution is determined only up to an arbitrary solution of the homogeneous equation

$$\hat{G}_0^{-1}(x)h(x, x') = 0. \qquad (43)$$

We shall discuss the problem of the unique choice of the solution and of the role of initial conditions later.

Equation (42) represents a system of four integro-differential equations. However, between the four unknown functions G_{ij} there exist two linear relations (33) and (34) which, naturally, are consistent with the equations. Therefore, by means of a certain linear canonical transformation of the matrices G, γ and D we can reduce the number of independent equations to two. Such a transformation is given by

$$G \rightarrow \frac{1 - i\sigma_y}{\sqrt{2}} \begin{pmatrix} G^c & G^- \\ G^+ & \tilde{G}^c \end{pmatrix} \frac{1 + i\sigma_y}{\sqrt{2}} = \begin{pmatrix} 0 & G^a \\ G^r & F \end{pmatrix}, \quad (44)$$

where three new Green's functions have been introduced: the advanced one G^a, the retarded one G^r, and the correlation function F which, as we shall see later, is essentially a single-particle density matrix. The matrix σ_y is the second of the three Pauli matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The functions G^a, G^r, and F are defined as follows in terms of average values of Heisenberg operators using the Heisenberg density matrix:

$$G^a(x, x') = -i\theta(t - t')\langle[\psi(x), \psi^+(x')]_+\rangle, \qquad (45)$$

$$G^r(x, x') = i\theta(t' - t)\langle[\psi(x), \psi^+(x')]_+\rangle, \qquad (46)$$

$$F(x, x') = -i\langle[\psi(x), \psi^+(x')]_-\rangle. \qquad (47)$$

They are related to the G-functions used above by means of the relations

$$G^a = G^c - G^+ = -\tilde{G}^c + G^-$$

$$= -\theta(t - t')(G^+ - G^-), \qquad (48)$$

$$G^r = G^c - G^- = -\tilde{G}^c + G^+$$

$$= \theta(t' - t)(G^+ - G^-), \qquad (49)$$

$$F = G^c + \tilde{G}^c = G^+ + G^-. \qquad (50)$$

The D-matrix transforms in a similar fashion. The vertex matrix γ_{ij}^k and the operator $\hat{G}_0^{-1}$ are also altered:

$$\gamma_{ij}{}^1 = 2^{-1/2}\delta_{ij}, \qquad \gamma_{ij}{}^2 = 2^{-1/2}(\sigma_x)_{ij}, \qquad (51)$$

$$\hat{G}_0^{-1} = \sigma_x G_0^{-1}(x). \qquad (52)$$

The self energy matrix Σ is brought to the form

$$\Sigma = \begin{pmatrix} \Omega & \Sigma^r \\ \Sigma^a & 0 \end{pmatrix}; \tag{53}$$

$$\Sigma^r = \Sigma^c + \Sigma^- = -(\widetilde{\Sigma}^c + \Sigma^+),$$
$$\Sigma^a = \Sigma^c + \Sigma^+ = -(\widetilde{\Sigma}^c + \Sigma^-),$$
$$\Omega = \Sigma^c + \widetilde{\Sigma}^c = -(\Sigma^+ + \Sigma^-). \tag{54}$$

The difference between (53), (54) and (44), (48)−(50) is related to the fact that the quantities $\Sigma^\pm$ in contrast to Σ^c and $\widetilde{\Sigma}^c$ contain the factor −1, which appears in the vertex (37) for k = 2, an odd number of times.

The general equations (39) and (42) are obviously invariant under the transformation (44); we simply go over to a new representation for the matrices G and D. But the number of independent equations is now obviously equal to two since the functions G^a and G^r are Hermitian conjugates and the equations for them follow from each other. The physical meaning of the functions G^r and F is quite different. Roughly speaking, G^r and G^a characterize the dynamic properties of the particles in the system under consideration, while F characterizes their static distribution. This can already be seen from the definition of these functions in the absence both of an external field and of an interaction, i.e., for t → −∞. Then, going over to Fourier transforms with respect to the differences $\mathbf{r} - \mathbf{r}'$ and $t - t'$ we obtain

$$G_0(\mathbf{p}\varepsilon) = \int G_0(\mathbf{r} - \mathbf{r}', t - t') \exp\{-i[\mathbf{p}(\mathbf{r} - \mathbf{r}')$$
$$- \varepsilon(t - t')]\} \, d(\mathbf{r} - \mathbf{r}') d(t - t') \tag{55}$$

and in the limiting case mentioned above

$$G_0^r(\mathbf{p}\varepsilon) = G_0^{a*}(\mathbf{p}\varepsilon) = 1/(\varepsilon - \varepsilon_\mathbf{p} - i\delta),$$
$$\delta \to +0, \tag{56}$$

$$G_0^+(\mathbf{p}\varepsilon) = 2\pi i n_\mathbf{p} \delta(\varepsilon - \varepsilon_\mathbf{p}),$$
$$G_0^-(\mathbf{p}\varepsilon) = -2\pi i(1 - n_\mathbf{p}) \delta(\varepsilon - \varepsilon_\mathbf{p}), \tag{57}$$

$$F_0(\mathbf{p}\varepsilon) = 2\pi i(2n_\mathbf{p} - 1) \delta(\varepsilon - \varepsilon_\mathbf{p}), \tag{58}$$

where

$$n_\mathbf{p} = \left[\exp\frac{\varepsilon_\mathbf{p} - \mu}{kT} + 1\right]^{-1}$$

is the Fermi distribution function, μ is the chemical potential in the equilibrium state. Thus, the functions F and $G^\pm$ essentially represent the distribution function for the particles written in different forms.

When the interaction is taken into account the

functions G^r and G^a also indirectly depend on the distribution of the particles, but the fact that $G^\pm(\mathbf{r}t, \mathbf{r}'t)$ and $F(\mathbf{r}t, \mathbf{r}'t)$ taken at coincident times $t' = t$ directly determine the distributions of electrons and of holes follows directly from their definition (32). We shall now show that the equation for G^+ (or the equation for F equivalent to it) contains within itself the usual Boltzmann kinetic equation under the assumptions under which the latter exists, i.e., when the external field is quasiclassical and the interaction is weak in the sense

$$\hbar/\tau \ll \bar{\varepsilon}, \tag{59}$$

where τ is the time taken to traverse a mean free path, and $\bar{\epsilon}$ is the average energy of the particles.

The equation for G^+ has the form

$$G_0^{-1}(x)G^+(x, x') = ig^2 \int \{\Sigma^+(x, x'')G^c(x'', x')$$
$$+ \widetilde{\Sigma}^c(x, x'')G^+(x'', x')\} \, dx''. \tag{60}$$

The corresponding Hermitian conjugate equation is

$$G_0^{-1*}(x')G^+(x, x') = ig^2 \int \{\widetilde{G}^c(x, x'')\Sigma^+(x'', x')$$
$$+ G^+(x, x'')\Sigma^c(x'', x')\} \, dx''. \tag{61}$$

We add these two equations, then go over from the variables x, x' to the new variables $(\mathbf{r}_s t_s) = x_s = (x + x')/2$ and $(\mathbf{r}_a t_a) = x_a = (x - x')/2$, and then take a Fourier transform of the type (55) with respect to the difference variable x_a. As a result terms of the type

$$ig^2 \int \Sigma(x_s + x_a', p')G(x_s - x_a + x_a', p'') \exp\{i[(p' - p)x_a$$
$$+ (p'' - p')x_a']\} \, dx_a dx_a' dp' dp'', \quad p = (\mathbf{p}\varepsilon),$$

will appear on the right hand side of the equation.

The quasiclassical nature of the external field means that quantities of the type $p\nabla_s$ are small. At the same time the right hand side of the equation is proportional to the small interaction constant g^2. Therefore, neglecting small terms of the form $g^2(p\nabla_s)$ and introducing a further change of variables $\mathbf{p} \to \mathbf{p} - e\mathbf{A}(x_s)/c$, $\epsilon \to \epsilon - e\Phi(x_s)$, we obtain

$$\left\{\frac{\partial}{\partial t_s} + \mathbf{v}_\mathbf{p}\nabla_s + \left(e\mathbf{E} + \left[\frac{e\mathbf{v}_\mathbf{p}}{c}\mathbf{H}\right]\right)\nabla_\mathbf{p}\right\} G^+(x_s p)$$
$$= g^2 \{\Sigma^+(x_s p) [G^c(x_s p) + \widetilde{G}^c(x_s p)]$$
$$+ [\Sigma^c(x_s p) + \widetilde{\Sigma}^c(x_s p)] G^+(x_s p)\}, \tag{62}*$$

where $\mathbf{v}_\mathbf{p} = \nabla_\mathbf{p}\epsilon_\mathbf{p}$ is the velocity of the particles, E and H are the electric and the magnetic fields:

_____
$*[\mathbf{v}_\mathbf{p}\,\mathbf{H}] = \mathbf{v}_\mathbf{p} \times \mathbf{H}.$

$$\mathbf{E} = -\nabla\Phi - c^{-1}\partial\mathbf{A}/\partial t; \qquad \mathbf{H} = \operatorname{rot}\mathbf{A}. \quad (63)*$$

In deriving (62) we have expanded in the left hand side of the equation the operator $G_0^{-1}(x) - G_0^{-1*}(x')$ in series in terms of the small difference $x_a = (x - x')/2$ up to the first order on the basis of the same quasiclassical condition. The right hand side of (62) can be further simplified by utilizing (50) and (54):

$$\left\{\frac{\partial}{\partial t} + \mathbf{v}\nabla + e\left(\mathbf{E} + \left[\frac{\mathbf{v}}{c}\mathbf{H}\right]\right)\nabla_{\mathbf{p}}\right\}G^+(xp)$$

$$= g^2\{\Sigma^+(xp)G^-(xp) - \Sigma^-(xp)G^+(xp)\}. \quad (64)$$

The right hand side of (64) describes the effect of collisions on the distribution of the particles, with the first term being related to particles entering the state of momentum $\mathbf{p}$ from all the other states with momenta $\mathbf{p}'$, while the second term is related to the particles leaving the state. In order to bring this equation to the usual form of the Boltzmann equation we introduce the distribution function $f(\mathbf{p}\mathbf{r}t)$ which, as has been noted previously, coincides with G^+ for coincident times $t' = t$:

$$f(\mathbf{p}\mathbf{r}t) = \frac{1}{2\pi i}\int_{-\infty}^{\infty}G^+(\mathbf{r}t;\ \mathbf{p}\varepsilon)\,d\varepsilon. \quad (65)$$

Integration of equation (64) over ϵ then yields

$$\left\{\frac{\partial}{\partial t} + \mathbf{v}\boldsymbol{\nabla} + e\left(\mathscr{E} + \left[\frac{\mathbf{v}}{c}\mathbf{H}\right]\right)\boldsymbol{\nabla}_{\mathbf{p}}\right\}f(\mathbf{p}\mathbf{r}t)$$

$$= \frac{g^2}{2\pi i}\int_{-\infty}^{\infty}\{\Sigma^+(\mathbf{r}t;\ \mathbf{p}\varepsilon)G^-(\mathbf{r}t;\ \mathbf{p}\varepsilon)$$

$$- \Sigma^-(\mathbf{r}t;\ \mathbf{p}\varepsilon)G^+(\mathbf{r}t;\ \mathbf{p}\varepsilon)\}\,d\varepsilon. \quad (66)$$

In accordance with the assumption that the interaction is small we must evaluate the right hand side of (66) up to the first order in g^2, i.e., we must substitute into (66) and (39) the functions $G_0^\pm$, satisfying the free equations

$$G_0^{-1}G_0^\pm(\mathbf{r}t;\ \mathbf{p}\varepsilon) = 0, \quad (67)$$

but normalized with respect to an as yet unknown distribution function f by equations (65) and (35). Symbolically they can be written in the form

$$G_0^+(\mathbf{r}t;\ \mathbf{p}\varepsilon) = 2\pi i\delta(\varepsilon - \varepsilon_{\mathbf{p}} + i\hat{B})f(\mathbf{p}\mathbf{r}t), \quad (68)$$

$$G_0^-(\mathbf{r}t;\ \mathbf{p}\varepsilon) = -2\pi i\delta(\varepsilon - \varepsilon_{\mathbf{p}} + i\hat{B})(1 - f(\mathbf{p}\mathbf{r}t)), \quad (69)$$

where $\hat{B}$ is the operator in the left hand side of (66). The quantity $\delta(G_0^{-1})$ in formulas (68), (69), is an integral operator with a kernel satisfying equation (67) and equal to $\delta(\mathbf{r} - \mathbf{r}')$ for $t' = t$. It can be easily expressed in terms of the functions $\varphi_{\mathbf{p}}$ (4).

*rot = curl.

In order to evaluate $\Sigma^\pm$ we must also define $D_0^\pm$. In the majority of problems of solid state physics the phonons can be regarded as being in thermodynamic equilibrium. Then

$$D_0^\pm(\mathbf{k}\omega) = -i\pi|m_{\mathbf{k}}|^2\{(1 + N_{\mathbf{k}})\delta(\omega \pm \omega_{\mathbf{k}})$$

$$+ N_{\mathbf{k}}\delta(\omega \mp \omega_{\mathbf{k}})\}, \quad (70)$$

where $\mathbf{k}$ and $\omega_{\mathbf{k}}$ are the propagation vector and the frequency of the phonon, $m_{\mathbf{k}}$ is the matrix element for the interaction with the electron, and

$$N_{\mathbf{k}} = \left[\exp\frac{\omega_{\mathbf{k}}}{kT} - 1\right]^{-1} \quad (71)$$

is the Planck distribution function.

Substituting (68)—(70) into (66) we obtain

$$\hat{B}f(\mathbf{p}\mathbf{r}t) = 2\pi^2 g^2\int|m_{\mathbf{k}}|^2\{[(1 + N_{\mathbf{k}})\delta(\varepsilon_{\mathbf{p}} - \varepsilon_{\mathbf{p}+\mathbf{k}} + \omega_{\mathbf{k}})$$

$$+ N_{\mathbf{k}}\delta(\varepsilon_{\mathbf{p}} - \varepsilon_{\mathbf{p}+\mathbf{k}} - \omega_{\mathbf{k}})]f(\mathbf{p} + \mathbf{k},\ \mathbf{r}t)(1 - f(\mathbf{p}\mathbf{r}t))$$

$$- [(1 + N_{\mathbf{k}})\delta(\varepsilon_{\mathbf{p}} - \varepsilon_{\mathbf{p}+\mathbf{k}} - \omega_{\mathbf{k}}) + N_{\mathbf{k}}\delta(\varepsilon_{\mathbf{p}} - \varepsilon_{\mathbf{p}+\mathbf{k}} + \omega_{\mathbf{k}})]$$

$$\times (1 - f(\mathbf{p} + \mathbf{k},\ \mathbf{r}t))f(\mathbf{p}\mathbf{r}t)\}\,d\mathbf{k}/(2\pi)^3, \quad (72)$$

i.e., the usual form of Boltzmann's equation. Thus, in deriving it we have utilized two conditions: the quasiclassical nature of the external field

$$\frac{d}{dx}(e\mathbf{A},\ e\Phi) \ll \varepsilon\bar{p} \quad (73)$$

and the smallness of the interaction

$$\bar{\varepsilon} \gg g^2\Sigma^\pm \sim \hbar/\tau. \quad (74)$$

The quasiclassical condition is not obligatory. Proceeding in exactly the same manner, but without expanding (60) and (61) in terms of the external field, we would have obtained the so-called quantum kinetic equation[16,17]. But the condition of smallness of the interaction (74) is necessary in this case also. If it is violated, then the functions $G^\pm$ do not have a δ-like character (68), (69) as functions of ϵ, and the integration over ϵ in equation (66) cannot be effectively carried out. In such a case we shall not obtain, generally speaking, a closed equation for the distribution function $f(\mathbf{p}\mathbf{r}t)$, i.e., for the G^+-function for coincident times $t' = t$. The equation exists only for the complete G-function considered as a function of all its arguments. In the most general case this corresponds to Dyson's equations (39) and (42). If the interaction is not weak, they can be solved if the system has some other parameters, for example density, which enable us to select a set of principal diagrams. However, in this case there will arise the previously mentioned problem of the nonuniqueness of the solution of (42) up to an arbitrary solution of the free equation. We shall now show that such

arbitrariness does not in fact exist, and that there is a unique prescription for the choice of the correct solution.

In order to do this we compare Eqs. (42) and (38) in the representation (44), by writing them separately for each of the functions G^a, G^r and F. In differential form

$$G_0^{-1}G^a = 1 + \Sigma^a G^a, \tag{75}$$

$$G_0^{-1}G^r = 1 + \Sigma^r G^r, \tag{76}$$

$$G_0^{-1}F = \Omega G^a + \Sigma^r F; \tag{77}$$

in integral form, corresponding to equation (38),

$$G^a = G_0^a(1 + \Sigma^a G^a), \tag{75a}$$

$$G^r = G_0^r(1 + \Sigma^r G^r), \tag{76a}$$

$$F = F_0(1 + \Sigma^a G^a) + G_0^r(\Omega G^a + \Sigma^r F). \tag{77a}$$

Comparison of (75)–(77) with (75a)–(77a) shows that equations (75), (76) do not contain any arbitrariness: they are solved by the advanced operator G_0^a or the retarded operator G_0^r respectively. For $t' \to t$ their solutions must go over into $\delta(\mathbf{r} - \mathbf{r}')$. A possible lack of uniqueness, i.e., dependence on initial conditions, is associated only with the term proportional to F_0 in equation (77a), since F_0 depends on the initial distribution, while in the differential form of the equation this term is completely absent. However, it can be easily seen that this term is identically equal to zero. Indeed, we substitute (75) into (77a). Then we have

$$F = F_0 G_0^{-1} G^a + G_0^r(\Omega G^a + \Sigma^r F) = G_0^r(\Omega G^a + \Sigma^r F), \tag{78}$$

since $F_0 G_0^{-1} = 0$. Thus, (77) is solved by means of the function G_0^r operating from the left. Equation (77) and its solution only appear to be nonsymmetric with respect to retarded and advanced functions. In place of (77) we can consider the Hermitian conjugate equation equivalent to it

$$G_0^{-1}F = G^r \Omega + F \Sigma^a, \tag{79}$$

which is solved by the function G_0^a operating from the right. Thus, solutions of Eqs. (75)–(77) are determined uniquely and independently of the initial distribution at $t = -\infty$.

We should now make clear to what systems the results obtained above are applicable. Evidently, we are dealing with well established solutions, i.e., such solutions which are determined by the effect of the external field at the present and at earlier instants of time, by the interaction with the heat bath, but not by the initial conditions. Generally speaking, these are not stationary solutions if the external field depends on the time. The lack of dependence on the initial conditions means physically that the initial conditions, even if they had been imposed, were specified in the sufficiently remote past, formally at $t \to -\infty$, while in fact we are dealing with times large in comparison to the relaxation time of the system. However, in discussions of kinetic phenomena, another way of posing the problem is possible: at time t_0 an arbitrary density matrix $\rho(t_0)$ is given and we are dealing with the relaxation of this state towards some well established regime. Such a problem, apparently, can not in principle be described by any diagram technique, since the latter is always based on the concept of the possibility of expressing two-, three-, etc. particle Green's functions in terms of the one-particle Green's function at least in the form of an infinite series. But an arbitrary specification of the density matrix is equivalent to an arbitrary and independent specification of all these quantities.

The existence of well established solutions independent of initial conditions is evident in the case of systems in contact with a heat bath. In the case of an adiabatic system the problem is less clear and the technique under discussion is applicable with certainty only in the case when the system had been actually in a state of thermodynamic equilibrium and was then taken out of that state by a given external field. The problem of approach to equilibrium from an arbitrary initial state has been discussed in papers by Van Hove[18], Prigogine and Resibois[19], Fujita[20] and others.

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