

KINETIC EQUATIONS FOR RELAXATION PROCESSES IN SUPERCONDUCTORS

V. P. GALAIKO

Physico-technical Institute, Ukrainian Academy of Sciences

Submitted January 1, 1971

Zh. Eksp. Teor. Fiz. 61, 382-397 (July, 1971)

We obtain a kinetic equation for the generalized electron density matrix of a superconductor. The relaxation of a system to an equilibrium state described by this equation takes place in two stages. First a fast quantal rearrangement of the system occurs; a self-consistent field of the superconducting condensate is formed and a quasi-particle description of the excitations is valid. After that the quasi-particle distribution and the superconducting ordering parameter slowly evolve due to collisions between the excitations.

AFTER a microscopic theory of superconductivity had been constructed^[1,2] various kinetic phenomena in superconductors (such as heat conductivity, ultrasound absorption, interaction with a weak electromagnetic field) were studied in the framework of the linear functions for the response of the system to a weak external influence (see, e.g.,^[3]). According to the generalized fluctuation-dissipation theorem^[4] the corresponding kinetic coefficients can in that case be expressed in terms of correlation functions for the equilibrium fluctuations of the system and can be evaluated by applying standard methods of quantum field theory to systems with a large number of degrees of freedom.^[5] A generalization of these methods to the case of essentially non-linear, non-stationary processes in superconductors (such as, e.g., the variable Josephson current,^[6] or resistive states in superconductors of the second kind^[7]) was proposed by Gor'kov and Éliashberg.^[8] Their procedure was based upon the analytical continuation of the electron Green functions of the superconductor which satisfy the Gor'kov equations,^[9] to the real frequency region.

The Green functions are a very general theoretical concept which enables us in principle to describe kinetic phenomena in condensed systems even when there is no sharp separation of the time scales (relaxation time) and the usual method of the kinetic equations is inapplicable. If, nevertheless, such a division is possible, the kinetic equations are much preferable, since they determine directly the temporal evolution of the physical parameters of the system like, for instance, the kinetic equation for the single-particle electron density matrix which is the basis of the evaluation of the kinetic phenomena in normal metals. However, in contrast to the kinetics of normal metals for a superconductor the choice of the parameters for a kinetic description just as the derivation of the kinetic equations themselves is not at all obvious and must be performed anew starting from first principles of statistics.

A necessary condition for a macroscopic description

¹⁾It is, however, necessary to note that the Gor'kov equations do not describe the relaxation of the electrons with respect to energy, since the electron-electron interaction is in them taken into account only to the extent in which it guarantees a non-zero value of the superconducting ordering parameter.

of non-stationary processes in the case of large deviations from equilibrium is that they proceed slowly in time. Thanks to that condition the statistical operator ρ which satisfies the quantal Liouville equation

$$i\partial\rho/\partial t = [\mathcal{H}, \rho], \quad (1)$$

can be synchronized with some set of macroscopic parameters γ_k , the temporal evolution of which is described by kinetic equations and as a result one can abbreviate the complete mechanical description of the system.^[10] Thus during the lapse of a short time interval τ_0 the following equations must be satisfied:

$$t \gg \tau_0, \quad \rho(t) = \rho(\gamma(t)), \quad \gamma_k = \text{Sp}(\rho \hat{\gamma}_k), \quad (2)$$

$$\partial\gamma_k/\partial t = L_k(\gamma). \quad (3)$$

Peletminskii and Yatsenko^[11] proposed a rather general scheme for deriving quantal kinetic equations in the above-mentioned sense for an extensive class of systems; they consider systems with a Hamiltonian \mathcal{H} which can be split into a "basic" Hamiltonian \mathcal{H}_0 guaranteeing the synchronization of the statistical operator with the parameters γ_k and a relatively weak interaction $V(\mathcal{H} = \mathcal{H}_0 + V)$ due to which the parameters γ_k relax to their equilibrium values. The choice of the parameters γ_k is determined by the symmetry properties of the Hamiltonian \mathcal{H}_0 and the main condition assumed in^[11] consists in that the corresponding operators $\hat{\gamma}_k$ must satisfy the commutation relations:

$$[\mathcal{H}_0, \hat{\gamma}_k] = \sum_i a_{ki} \hat{\gamma}_i. \quad (4)$$

The conditions (4) are the natural linear generalization of the usual commutation relations $[\mathcal{H}_0, \hat{\gamma}_k] = 0$ (conservation laws) and enable us to describe the system with a self-consistent field. In particular, as we shall show in this paper, similar relations can be used as a basis to derive kinetic equations also for superconductors since the BCS theory of superconductivity^[11] is a variant of a self-consistent field theory.

1. DERIVATION OF THE KINETIC EQUATIONS

It is well known^[1] that the phenomenon of superconductivity of metals is connected with the fact that thanks to the effective attraction between electrons induced by

the electron-phonon interaction there occur characteristic correlations of electron pairs with antiparallel momenta and spins. The corresponding rearrangement of the electron states involves a narrow layer with a width of the order of T_c (T_c is the superconducting transition temperature) near the Fermi boundary. It is therefore sufficient for the construction of a kinetic theory of the superconducting state to consider only the dynamics of the electrons in that layer assuming that the fast process of Fermi-occupation has essentially already been accomplished.

This observation enables us to simplify considerably the Hamiltonian of the system under consideration. In particular, we can assume the dispersion law for the electrons to be given and, for the sake of simplicity, we can put $\mathcal{E}(p) = p^2/2m$. Moreover, as the characteristic frequency determining the interaction of the electrons through the field of the virtual phonons is of the order of the Debye frequency ω_D in the weak coupling approximation ($T_c \ll \omega_D$) we can neglect the retardation of this interaction and we can thus use for the Hamiltonian of the system the Gor'kov model:^[9]

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_0 + \mathcal{H}_{int}, \\ \mathcal{H}_0 &= \int dV [\psi_{\uparrow}^{\dagger} (\mathcal{E}(\hat{p} - eA) + u) \psi_{\uparrow} + \psi_{\downarrow}^{\dagger} (\mathcal{E}(\hat{p} - eA) + u) \psi_{\downarrow}], \\ \mathcal{H}_{int} &= g \int dV (\psi_{\uparrow}^{\dagger} \psi_{\downarrow}^{\dagger} \psi_{\downarrow} \psi_{\uparrow}), \\ \mathcal{E}(p) &= p^2/2m, \quad \hat{p} = -i\nabla \quad (\hbar = 1, c = 1), \end{aligned} \quad (5)$$

where $\psi_{\uparrow}(\mathbf{r})$, $\psi_{\downarrow}(\mathbf{r})$, $\psi_{\uparrow}^{\dagger}(\mathbf{r})$, and $\psi_{\downarrow}^{\dagger}(\mathbf{r})$ are the annihilation and creation operators of electrons with a given spin at the point \mathbf{r} , $g < 0$ is a small constant for the effective attraction of the electrons acting near the Fermi boundary in a layer with a thickness of order ω_D , $A(\mathbf{r}, t)$ is the vector potential of the electromagnetic field. The potential $u(\mathbf{r}, t)$ includes the scalar potential of the electromagnetic field and also the interaction with other external fields, impurities, and so on.

Turning now to the condition (4) we note easily that apart from the usual quantities $\psi_{\uparrow}^{\dagger}(\mathbf{r}_1) \psi_{\uparrow}(\mathbf{r}_2)$, $\psi_{\downarrow}^{\dagger}(\mathbf{r}_1) \psi_{\downarrow}(\mathbf{r}_2)$ from which the single-particle density matrix for normal electrons is constructed, Eqs. (4) are also satisfied by the operators $\psi_{\uparrow}^{\dagger}(\mathbf{r}_1) \psi_{\downarrow}(\mathbf{r}_2)$ and $\psi_{\downarrow}^{\dagger}(\mathbf{r}_1) \psi_{\uparrow}(\mathbf{r}_2)$. It is well known^[1, 2, 9] that the occurrence of non-zero average values of these quantities is a characteristic property of the superconducting electron gas and reflects the appearance of correlations of electron pairs with antiparallel spins (electron-hole correlations). The more complete set of the quantities $\psi_{\uparrow}^{\dagger}(\mathbf{r}_1) \psi_{\uparrow}(\mathbf{r}_2)$, $\psi_{\downarrow}^{\dagger}(\mathbf{r}_1) \psi_{\downarrow}(\mathbf{r}_2)$, $\psi_{\uparrow}^{\dagger}(\mathbf{r}_1) \psi_{\downarrow}(\mathbf{r}_2)$, and $\psi_{\downarrow}^{\dagger}(\mathbf{r}_1) \psi_{\uparrow}(\mathbf{r}_2)$ must thus be the set of parameters $\hat{\gamma}$ for a superconductor and give us a kinetic description of the superconducting state. In the coordinate representation these quantities are in a natural way combined in the matrix:

$$\hat{\gamma}(\mathbf{r}_1, \mathbf{r}_2) = \begin{pmatrix} \psi_{\uparrow}^{\dagger}(\mathbf{r}_1) \psi_{\uparrow}^{\dagger}(\mathbf{r}_2) & \psi_{\uparrow}^{\dagger}(\mathbf{r}_1) \psi_{\downarrow}(\mathbf{r}_2) \\ \psi_{\downarrow}^{\dagger}(\mathbf{r}_1) \psi_{\uparrow}^{\dagger}(\mathbf{r}_2) & \psi_{\downarrow}^{\dagger}(\mathbf{r}_1) \psi_{\downarrow}(\mathbf{r}_2) \end{pmatrix}, \quad \hat{\gamma}^{\dagger} = \hat{\gamma}. \quad (6)$$

It is convenient in connection of the given matrix description to use in what follows the absence of spin interactions in the Hamiltonian \mathcal{H} of (5) and introduce new canonical annihilation and creation operators of electrons and holes which formally form vectors, using the equations

$$\begin{pmatrix} \varphi_{\uparrow} \\ \varphi_{\downarrow} \end{pmatrix} = \begin{pmatrix} \psi_{\uparrow} \\ \psi_{\downarrow} \end{pmatrix}, \quad (\varphi_{\uparrow}^{\dagger} \varphi_{\downarrow}^{\dagger}) = (\psi_{\uparrow}^{\dagger} \psi_{\downarrow}^{\dagger}),$$

$$\begin{aligned} \{\varphi_{\alpha}(\mathbf{r}), \varphi_{\beta}^{\dagger}(\mathbf{r}')\} &\equiv \varphi_{\alpha}(\mathbf{r}) \varphi_{\beta}^{\dagger}(\mathbf{r}') + \varphi_{\beta}^{\dagger}(\mathbf{r}') \varphi_{\alpha}(\mathbf{r}) = \delta_{\alpha\beta} \delta(\mathbf{r} - \mathbf{r}'), \\ \{\varphi_{\alpha}(\mathbf{r}), \varphi_{\beta}(\mathbf{r}')\} &= \{\varphi_{\alpha}^{\dagger}(\mathbf{r}), \varphi_{\beta}^{\dagger}(\mathbf{r}')\} = 0. \end{aligned} \quad (7)$$

In that case $\hat{\gamma}$ of (6) can be written as follows:

$$\hat{\gamma}_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = \varphi_{\alpha}(\mathbf{r}_1) \varphi_{\beta}^{\dagger}(\mathbf{r}_2). \quad (8)$$

Consequently the Hamiltonians \mathcal{H}_0 and \mathcal{H}_{int} of (5) can, apart from a c-number, after some simple transformations be written as:

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_0 + \mathcal{H}_{int}; \quad \mathcal{H}_0 = \int dV (\varphi^{\dagger} \sigma_z \mathcal{E}(\hat{p} - \sigma_z eA) + \sigma_z u, \varphi), \\ \mathcal{H}_{int} &= g \int dV (\varphi^{\dagger} \sigma_x \varphi) (\varphi^{\dagger} \sigma_y \varphi), \quad \sigma_{\pm} = 1/2 (\sigma_x \pm i\sigma_y), \end{aligned} \quad (9)$$

where σ_x , σ_y , σ_z are Pauli matrices.

To find the explicit form of the functional $\rho(\gamma)$ of (2) and the kinetic equations (3) describing the temporal evolution of the parameters γ it is necessary to solve the integral Eqs. (21) of ^[11] written so as to be applicable to the present case, using Eqs. (7), (8), and (9).

These equations can for the case of a normal metal be solved immediately using perturbation theory. It is well known^[11] that in the case of a superconductor, notwithstanding the smallness of the interaction \mathcal{H}_{int} , perturbation theory is inapplicable and it is necessary to work out an appropriate method to solve these equations, which would take into account the effects of the pairing of the superconducting electrons. It is, however, more convenient to proceed slightly differently and to derive anew the equations of ^[11], regrouping the terms in the Hamiltonian \mathcal{H} of (9) in such a way that we can apply perturbation theory to the equations obtained. To do this we note that for electrons near the Fermi surface no interaction will formally be weak because the excitation energy is small. The interaction Hamiltonian \mathcal{H}_{int} can thus contain "dangerous" terms which have a large effect on the electron states near the Fermi boundary. These terms can be split off in the spirit of the generalized Hartree-Fock approximation in a way similar to what was done in ^[2] to compensate the "dangerous" diagrams of the equilibrium perturbation theory. We have thus

$$\begin{aligned} \mathcal{H}_{int}^{(0)} &= g \int dV [(\overline{\varphi^{\dagger} \sigma_x \varphi}) (\overline{\varphi^{\dagger} \sigma_y \varphi}) + (\overline{\varphi^{\dagger} \sigma_x \varphi}) (\overline{\varphi^{\dagger} \sigma_z \varphi}) + (\overline{\varphi^{\dagger} \sigma_x \varphi}) (\overline{\varphi^{\dagger} \sigma_x \varphi}) \\ &+ (\overline{\varphi^{\dagger} \sigma_x \varphi}) (\overline{\varphi^{\dagger} \sigma_y \varphi})] = g \int dV [-\text{Tr}(\sigma_x \gamma(\mathbf{r}, \mathbf{r})) (\overline{\varphi^{\dagger} \sigma_y \varphi}) - \text{Tr}(\sigma_y \gamma(\mathbf{r}, \mathbf{r})) (\overline{\varphi^{\dagger} \sigma_x \varphi}) \\ &+ (\overline{\varphi^{\dagger} \sigma_x \gamma(\mathbf{r}, \mathbf{r}) \sigma_y \varphi}) + \overline{\varphi^{\dagger} \sigma_x \varphi} (\sigma_x)_{\alpha\beta} \varphi_{\beta} \varphi_{\alpha}^{\dagger} (\sigma_x)_{\gamma\delta}]. \end{aligned} \quad (10)$$

The symbol $\overline{}$ denotes here the pairing of operators in the sense of Wick's theorem and Tr is the trace over the spin indices.

After regrouping the terms the Hamiltonian \mathcal{H} of (9) has the form

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_0(\gamma) + V(\gamma), \\ \mathcal{H}_0(\gamma) &= \mathcal{H}_0 + \mathcal{H}_{int}^{(0)}(\gamma), \quad V(\gamma) = \mathcal{H}_{int} - \mathcal{H}_{int}^{(0)}(\gamma). \end{aligned} \quad (11)$$

The Hamiltonian $V(\gamma)$ in (11) can now be considered to be a small uncompensated interaction which guarantees the relaxation of the system to an equilibrium state. It is necessary to emphasize that the validity of the splitting off of the "dangerous" terms in the form (10) is in fact confirmed in what follows by the fact that the "remaining" interaction $V(\gamma)$ leads only to a collision inte-

gral in the kinetic equation (3) which is quadratic in the coupling constant g and secular terms are thus eliminated in that equation.

Simple simplifications in Eqs. (9) and (10) lead to the following expression for the "basic" Hamiltonian $\mathcal{H}_S(\gamma)$:

$$\mathcal{H}_S(\gamma) = \int dV(\varphi^+, h_r(\gamma), \varphi), \quad (12)$$

where $h_r(\gamma)$ is a Hermitian matrix defined by the equations

$$h_r(\gamma) = \sigma_r \mathcal{E}(\hat{p} - \sigma_r eA(\mathbf{r})) + \sigma_r u(\mathbf{r}) + \hat{\zeta}(\mathbf{r}) + \hat{\Delta}(\mathbf{r});$$

$$\hat{\zeta}(\mathbf{r}) = \begin{pmatrix} gn_{\uparrow}(\mathbf{r}) & 0 \\ 0 & -gn_{\downarrow}(\mathbf{r}) \end{pmatrix} = \quad (13)$$

$$= \begin{pmatrix} g \text{Sp}(\rho\varphi_{-i}(\mathbf{r})\varphi_{-i}^+(\mathbf{r})) & 0 \\ 0 & -g \text{Sp}(\rho\varphi_{i}^+(\mathbf{r})\varphi_i(\mathbf{r})) \end{pmatrix},$$

$$\hat{\Delta}(\mathbf{r}) = |g|[\sigma_r \text{Tr}(\sigma_r \gamma(\mathbf{r}, \mathbf{r})) + \sigma_r \text{Tr}(\sigma_r \gamma(\mathbf{r}, \mathbf{r}))], \quad (14)$$

or, in the usual notation

$$h_r(\mathbf{r}) = \begin{pmatrix} \mathcal{E}(\hat{p} - eA(\mathbf{r})) + u(\mathbf{r}) + gn_{\uparrow}(\mathbf{r}), & \Delta(\mathbf{r}) \\ \Delta^*(\mathbf{r}), & -\mathcal{E}(\hat{p} + eA(\mathbf{r})) - u(\mathbf{r}) - gn_{\downarrow}(\mathbf{r}) \end{pmatrix},$$

$$\Delta(\mathbf{r}) = |g| \text{Tr}(\sigma_r \gamma(\mathbf{r}, \mathbf{r})), \quad \Delta^*(\mathbf{r}) = |g| \text{Tr}(\sigma_r \gamma(\mathbf{r}, \mathbf{r})). \quad (15)$$

By using Eqs. (12), (7), and (8) one can then easily check that the operator $\hat{\gamma}$ satisfies a linear condition of the form (4) also with respect to the Hamiltonian $\mathcal{H}_S(\gamma)$, viz.:

$$[\mathcal{H}_S(\gamma), \hat{\gamma}] = -[h(\gamma), \hat{\gamma}]_r, \quad h(\mathbf{r}_1, \mathbf{r}_2; \gamma) = h_r(\gamma) \delta(\mathbf{r}_1 - \mathbf{r}_2). \quad (16)$$

The index r of the commutator $[]_r$ on the right-hand side of Eq. (16) distinguishes the commutation of the matrices $h(\mathbf{r}_1, \mathbf{r}_2)$ and $\gamma(\mathbf{r}_1, \mathbf{r}_2)$ from the commutation of the operators \mathcal{H}_S and $\hat{\gamma}$.

The further derivation of the basic equations is completely similar to the derivation in ^[11] and is briefly reproduced here in view of the fact that Eqs. (16) formally differ somewhat from condition (4) because the matrix h depends on γ . It follows from Eqs. (1), (2), and (3) that the functional $\rho(\gamma)$ and the right-hand side of the kinetic equations (3) $L(\gamma)$ are defined by the following equations:

$$\text{Sp}_r \left(L(\gamma) \frac{\partial \rho(\gamma)}{\partial \gamma} \right) - i[\rho(\gamma), \mathcal{H}] = 0, \quad (17)$$

$$L(\gamma) = i \text{Sp}(\rho(\gamma) [\mathcal{H}, \hat{\gamma}]), \quad (18)$$

where Sp_r indicates a trace of a matrix in contrast to Sp for operators. We must add to Eq. (17) boundary conditions taking into account the irreversible character of the change in ρ .

When there are no interactions ($V(\gamma) = 0$) we have from (18) and (16)

$$L^{(0)}(\gamma) = i \text{Sp}(\rho(\gamma) [\mathcal{H}_S(\gamma), \hat{\gamma}]) = -i[h(\gamma), \gamma]_r. \quad (19)$$

We introduce the operator $S_T^{(0)}(\gamma)$ for the evolution of γ which is determined by $L^{(0)}(\gamma)$:²⁾

$$\frac{\partial}{\partial \tau} S_T^{(0)}(\gamma) = L^{(0)}(S_T^{(0)}(\gamma)), \quad S_T^{(0)}(\gamma)|_{\tau=0} = \gamma, \quad (20)$$

$$S_T^{(0)}(S_T^{(0)}(\gamma)) = S_{T+\tau}^{(0)}(\gamma).$$

In the absence of interactions ($V(\gamma) = 0$) the Liouville equation (1) can then be written in the following form:

$$i\partial_\rho(\tau)/\partial\tau = [\mathcal{H}_S(S_T^{(0)}(\gamma)), \rho(\tau)].$$

The formal solution of this equation with the boundary condition $\rho(\tau)|_{\tau=0} = \rho(\gamma)$ has the form

$$\rho(\tau) = U(\tau, 0; \gamma) \rho(\gamma) U^+(\tau, 0; \gamma), \quad (21)$$

where the integral operator U is determined from the equations

$$i \frac{\partial}{\partial \tau_2} U(\tau_2, \tau_1; \gamma) = \mathcal{H}_S(S_{\tau_2}^{(0)}(\gamma)) U(\tau_2, \tau_1; \gamma), \quad U(\tau, \tau; \gamma) = 1, \quad (22)$$

$$UU^+ = 1, \quad U(\tau_2, \tau; \gamma) U(\tau, \tau_1; \gamma) = U(\tau_2, \tau_1; \gamma).$$

According to the basic assumption (2) about the synchronization, the solution (21) must satisfy the following asymptotic relation:

$$\tau \rightarrow \infty, \quad U(\tau, 0; \gamma) \rho(\gamma) U^+(\tau, 0; \gamma) \rightarrow \rho^{(0)}(S_T^{(0)}(\gamma)), \quad (23)$$

where we must take for the operator $\rho^{(0)}(\gamma)$, as was shown in ^[11], the solution of Eq. (17) with $V(\gamma) = 0$, which can be obtained by coarse-graining by means of the "basic" Hamiltonian $\mathcal{H}_S(\gamma)$, i.e., a Gibbs distribution with fixed parameters γ :³⁾

$$\rho^{(0)}(\gamma) = \exp[\Omega - \text{Sp}_r(X(\gamma)\hat{\gamma})], \quad (24)$$

$$\text{Sp} \rho^{(0)}(\gamma) = 1, \quad \gamma = \text{Sp}(\rho^{(0)}(\gamma)\hat{\gamma}).$$

Using the easily proved identity

$$U(\tau_2, \tau_1; S_T^{(0)}(\gamma)) = U(\tau_2 + \tau, \tau_1 + \tau; \gamma) \quad (25)$$

and replacing in Eq. (23) $\gamma \rightarrow S_T^{(0)}(\gamma)$ we obtain finally the following boundary condition for Eq. (17):

$$\tau \rightarrow -\infty, \quad U(0, \tau; \gamma) \rho(S_T^{(0)}(\gamma)) U^+(0, \tau; \gamma) \rightarrow \rho^{(0)}(\gamma). \quad (26)$$

In connection with the definitions (20) and (22) we note the transformation law of the quantity $\hat{\gamma}$ under the action of the operator U :

$$U^+(\tau_2, \tau_1; \gamma) \hat{\gamma} U(\tau_2, \tau_1; \gamma) = S(\tau_2, \tau_1; \gamma) \hat{\gamma} S^+(\tau_2, \tau_1; \gamma), \quad (27)$$

where by virtue of Eqs. (22) and (16) the unitary matrix S is determined by equations analogous to (22):

$$i \frac{\partial}{\partial \tau_2} S(\tau_2, \tau_1; \gamma) = h(S_{\tau_2}^{(0)}(\gamma)) S(\tau_2, \tau_1; \gamma), \quad S(\tau, \tau; \gamma) = 1, \quad (28)$$

$$SS^+ = 1, \quad S(\tau_2, \tau; \gamma) S(\tau, \tau_1; \gamma) = S(\tau_2, \tau_1; \gamma),$$

where, according to Eqs. (19) and (20) the following relation holds:

$$S_T^{(0)}(\gamma) = S(\tau, 0; \gamma) \gamma S^+(\tau, 0; \gamma). \quad (29)$$

From (27), (28), and (29) we obtain the transformation law for the operator $\rho^{(0)}(\gamma)$ of (24):

$$U(\tau, 0; \gamma) \rho^{(0)}(\gamma) U^+(\tau, 0; \gamma) = \rho^{(0)}(S_T^{(0)}(\gamma)). \quad (30)$$

To solve Eq. (17), we change it into an integral equation using the boundary condition (26). Making the sub-

²⁾We note that the explicit time dependence of the Hamiltonian \mathcal{H}_S through the external fields A and u is unimportant for the further discussions since the characteristic frequencies of these fields must be rather low in order that the main synchronization condition (2) be satisfied.

³⁾One verifies easily by means of Eqs. (16) that $\rho^{(0)}(\gamma)$ in the form (24) indeed satisfies Eq. (17) with $V(\gamma) = 0$.

stitution $\gamma \rightarrow S_T^{(0)}(\gamma)$ in (17) and using the definition (20) we get

$$\frac{\partial}{\partial \tau} \rho(S_T^{(0)}(\gamma)) - i[\rho(S_T^{(0)}(\gamma)), \mathcal{H}_e(S_T^{(0)}(\gamma))] = f(S_T^{(0)}(\gamma)), \quad (31)$$

$$f(\gamma) = i[\rho(\gamma), V(\gamma)] - \text{Sp}_r \left[(L(\gamma) - L^{(0)}(\gamma)) \frac{\partial \rho(\gamma)}{\partial \gamma} \right]. \quad (32)$$

The integration of Eq. (31), using Eqs. (22), (25), and (30) and the boundary condition (26), gives

$$\rho(\gamma) = \rho^{(0)}(\gamma) + \int_{-\infty}^0 d\tau e^{iU(0, \tau; \gamma)} f(S_T^{(0)}(\gamma)) U^+(0, \tau; \gamma), \quad \eta \rightarrow +0. \quad (33)$$

We can check, as in [11], the self-consistency of the whole construction, i.e., prove by means of Eqs. (33), (27), (18), and (19) the following identity:

$$\gamma = \text{Sp}(\rho(\gamma)\hat{\gamma}) = \text{Sp}(\rho^{(0)}(\gamma)\hat{\gamma}). \quad (34)$$

Equations (33) and (32) together with the definitions (18) and (19) are the integral equations required to find $\rho(\gamma)$ and $L(\gamma)$. According to what we have said earlier the solution of these equations can be found by perturbation theory. The statistical averages over the distribution $\rho^{(0)}(\gamma)$ of (24) which then occur must clearly be evaluated using Wick's theorem, maintaining the matrix order of multiplication of the averaged quantities.

In the first order of perturbation theory we get from Eq. (18), using (34) and (16), the expression

$$L^{(1)}(\gamma) = i \text{Sp}(\rho^{(0)}(\gamma)[V(\gamma), \hat{\gamma}]) = i \langle [\mathcal{H}_{int} - \mathcal{H}_{int}^{(0)}(\gamma), \hat{\gamma}] \rangle.$$

Performing the standard calculations of commutators (Eqs. (7) to (10)) and substituting the results in the last expression we get after averaging

$$L^{(1)}(\gamma) = 0. \quad (35)$$

The next important term in the kinetic equations (3) is thus the "collision integral" $L^{(2)}(\gamma)$, which is quadratic in the interaction constant g . Using the identity (18) and Eq. (16), we have from (18)

$$L^{(2)}(\gamma) = i \text{Sp}(\rho^{(1)}(\gamma)[V(\gamma), \hat{\gamma}]) = i \text{Sp}(\rho^{(1)}(\gamma)[\mathcal{H}_{int}, \hat{\gamma}]). \quad (36)$$

By virtue of Eq. (35), $\rho^{(1)}(\gamma)$ is then determined according to Eqs. (33), (32), and (30) by the following equation:

$$\rho^{(1)}(\gamma) = i \int_{-\infty}^0 d\tau e^{iU(0, \tau; \gamma)} V(S_T^{(0)}(\gamma)) U^+(0, \tau; \gamma), \quad \eta \rightarrow +0 \quad (37)$$

After substituting this expression into Eq. (36) for $L^{(2)}(\gamma)$, it is useful for the further calculations of the subsequent statistical averages to bear in mind the compensating property of the Hamiltonian $H_{int}^{(0)}$ of (10) (see Eq. (35)). By direct calculation one can check that this property leads in the present case to the following simplification: we must omit $\mathcal{H}_{int}^{(0)}$ from Eq. (37) and when evaluating the averages forget about the pairing of operators according to Wick's theorem inside the Hamiltonian \mathcal{H}_{int} . $L^{(2)}(\gamma)$ of (36) thus has the form

$$L^{(2)}(\gamma) = - \int_{-\infty}^0 d\tau e^{iU(0, \tau; \gamma)} \overline{[\mathcal{H}_{int} U(0, \tau; \gamma), [\mathcal{H}_{int}, \hat{\gamma}]]}, \quad \eta \rightarrow +0, \quad (38)$$

where the symbol $\overline{\quad}$ indicates that one should pair the operators only of the two indicated terms, while the angle brackets $\langle \quad \rangle$ indicate statistical averaging with the operator $\rho^{(0)}(\gamma)$ of (24). The law for the transformation of the operators $\varphi(\mathbf{r})$ and $\varphi^+(\mathbf{r})$ in H_{int} in (9), effected

by the unitary operator U , can easily be established as before (see (27) and (28)) using (22), (12), (13), and (7).

We do not need in what follows the general form (38) of the "collision integral" $L^{(2)}(\gamma)$. The kinetic equation for the generalized density matrix γ thus has the form (see Eqs. (3), (19), (13), (16), and (35))

$$i \partial \gamma / \partial t = [h(\gamma), \gamma] + iL^{(2)}(\gamma). \quad (39)$$

2. RELAXATION PROCESSES LEADING TO THE EQUILIBRIUM STATE

Equation (39) enables us in principle to follow the transition of a system of electrons from an arbitrary initial state⁴⁾ into a final—superconducting or normal—equilibrium state. According to the derivation of Eq. (39) given in the first section, the "collision integral" $L^{(2)}(\gamma)$ is in general small compared with the first term in this equation. Accordingly the relaxation process for the matrix γ contains fast changes in time, determined by the first term, and a slow change due to the "collision integral" $L^{(2)}(\gamma)$. Turning to a detailed study of these processes we note first of all that the substitution $\gamma \rightarrow \exp\{-i\sigma_z \mu t\} \gamma \exp\{i\sigma_z \mu t\}$ leaves the form of this equation invariant and only shifts the zero of the energy $\mathcal{E}(\mathbf{p})$ of the electron by an amount μ . This property is clearly connected with the conservation of particle number in the system (more generally, with the gauge invariance of the theory), and this substitution constitutes in fact the separation of the chemical potential of the system in Eq. (39) in explicit form. In this connection it is convenient to separate the phase of the ordering parameter $\hat{\Delta}$ of (14):

$$\hat{\Delta} \rightarrow \exp(i\sigma_x \chi / 2) \sigma_x \Delta \exp(-i\sigma_x \chi / 2), \quad \Delta^* = \Delta, \quad (40)$$

$$\gamma(\mathbf{r}_1, \mathbf{r}_2) \rightarrow \exp(i\sigma_x \chi(\mathbf{r}_1) / 2) \gamma(\mathbf{r}_1, \mathbf{r}_2) \exp(-i\sigma_x \chi(\mathbf{r}_2) / 2).$$

After simple transformations we can then write Eq. (39) in the following form:

$$i \partial \gamma / \partial t = [\hat{\epsilon}(\gamma), \gamma] + iL^{(2)}(\gamma), \quad (41)$$

where the matrix $\hat{\epsilon}(\gamma)$ is determined by the relations

$$\hat{\epsilon}(\mathbf{r}_1, \mathbf{r}_2; \gamma) = \hat{\epsilon}_{r_1}(\gamma) \delta(\mathbf{r}_1 - \mathbf{r}_2); \quad (42)$$

$$\hat{\epsilon}_{r_1}(\gamma) = \sigma_r \left[\mathcal{E}(\hat{\mathbf{p}} + \sigma_r \mathbf{p}, (\mathbf{r})) + u(\mathbf{r}) + \frac{1}{2} \frac{\partial \chi(\mathbf{r})}{\partial t} \right] + \hat{\xi}(\mathbf{r}) + \sigma_z \Delta(\mathbf{r}),$$

$$\mathbf{p}, (\mathbf{r}) = \frac{1}{2} (\nabla \chi(\mathbf{r}) - 2e\mathbf{A}(\mathbf{r})) = m\mathbf{v}, (\mathbf{r}), \quad \Delta(\mathbf{r}) = \frac{1}{2} |g| \text{Tr}(\sigma_x \gamma(\mathbf{r}, \mathbf{r})). \quad (43)$$

The phase $\chi(\mathbf{r}, t)$ is determined by the condition that the parameter Δ be real, i.e., according to Eq. (15), by the equation

$$\text{Tr}(\sigma_y \gamma(\mathbf{r}, \mathbf{r})) = 0. \quad (44)$$

One can show that this latter equation is equivalent to the law of the conservation of particle number in the system:

$$\frac{\partial n}{\partial t} + \text{div } \mathbf{j} = 0,$$

$$n(\mathbf{r}) = \text{Tr}[\frac{1}{2} \delta(\mathbf{r} - \mathbf{r}') - \sigma_y \gamma(\mathbf{r}, \mathbf{r}')]_{r=r'},$$

$$\mathbf{j}(\mathbf{r}) = n(\mathbf{r}) \mathbf{v}, (\mathbf{r}) + \frac{\hat{\mathbf{p}} - \hat{\mathbf{p}}'}{2m} \text{Tr} \left[\frac{1}{2} \delta(\mathbf{r} - \mathbf{r}') - \gamma(\mathbf{r}, \mathbf{r}') \right]_{r=r'}.$$

⁴⁾As was shown earlier the initial conditions for Eq. (39) must refer to a class of electron distributions close to the normal one apart from a narrow layer (thickness $\sim T_c$) near the Fermi boundary.

The form of the "collision integral" $L^{(2)}(\gamma)$ of (38) in Eq. (41) remains formally as before. It is only necessary to replace in Eqs. (22), which define the unitary operator $U(\tau, 0; \gamma)$, the Hamiltonian $\mathcal{H}_S(\gamma)$ of (12) by the following:

$$\mathcal{H}_s(\gamma) = \int dV (\varphi^\dagger, \hat{\varepsilon}_r(\gamma), \varphi). \quad (45)$$

The fast changes of the matrix γ are now according to (41) described by the following equation:⁵⁾

$$i \partial \gamma / \partial t = [\hat{\varepsilon}(\gamma), \gamma], \quad (46)$$

and also by the self-consistency equations (43) and (44). From this equation it follows that the evolution of the matrix γ reduces to a unitary rotation. In the general spatially non-uniform case we cannot follow this evolution in detail for an arbitrary initial condition because Eqs. (46) and (43) are non-linear. However, in actual fact only the matrix γ averaged in a well-defined way has a physical meaning since all physical quantities are expressed through the trace with that matrix. We can, however, always state that after the lapse of a certain period of time the averaged matrix is diagonalized in the representation of the energy operator $\hat{\varepsilon}$. The time scale τ_1 after which this diagonalization is realized is determined by the characteristic energies ϵ and the class of initial conditions for γ . If we restrict ourselves to those conditions which were mentioned in footnote 4, then we have, in order of magnitude, $\tau_1 \sim 1/T_0$. Thus, when $t \gg \tau_1$ the matrix γ is asymptotically equivalent to the following one:

$$\gamma = \sum_{\lambda} \varphi_{\lambda} E_{\lambda} \quad ([\hat{\varepsilon}(\gamma), \gamma] = 0), \quad (47)$$

where the E_{λ} are projection operators constituting the expansion of unity for the Hermitian operator $\hat{\varepsilon}$:

$$\hat{\varepsilon} = \sum_{\lambda} \varepsilon_{\lambda} E_{\lambda}, \quad E_{\lambda} E_{\lambda'} = \delta_{\lambda\lambda'} E_{\lambda}, \quad (48)$$

$$E_{\lambda}(\mathbf{r}_1, \mathbf{r}_2) = |\mathbf{r}_1, \lambda\rangle \langle \lambda, \mathbf{r}_2|.$$

Here $|\mathbf{r}, \lambda\rangle$ is the normalized eigenvector of the operator $\hat{\varepsilon}_{\mathbf{r}}$ of (42):

$$\hat{\varepsilon}_{\mathbf{r}} |\mathbf{r}, \lambda\rangle = \varepsilon_{\lambda} |\mathbf{r}, \lambda\rangle. \quad (49)$$

The self-consistency equations then become

$$\Delta(\mathbf{r}) = |g| \sum_{\lambda} \frac{1}{2} \text{Tr}(\sigma_x |\mathbf{r}, \lambda\rangle \langle \lambda, \mathbf{r}|) \varphi_{\lambda}, \quad (50)$$

$$0 = |g| \sum_{\lambda} \frac{1}{2} \text{Tr}(\sigma_y |\mathbf{r}, \lambda\rangle \langle \lambda, \mathbf{r}|) \varphi_{\lambda}.$$

As a result we can further simplify the description: the system is now described by the excitation distribution functions φ_{λ} and the superconducting ordering parameter Δ satisfying the self-consistent field Eqs. (50) with non-equilibrium distribution function.

The further slow change of the distribution function φ_{λ} and the parameter Δ is determined by the "collision integral" $L^{(2)}(\gamma)$. To find the explicit form of the equations describing the slow evolution of the functions φ_{λ} we may assume that in the basic kinetic equation (41) the relaxation process determined by the term

$[\hat{\varepsilon}(\gamma), \gamma]$ is completed and that thus, as to order of magnitude,

$$i \partial \gamma / \partial t \sim i L^{(2)}(\gamma) \ll [\hat{\varepsilon}(\gamma), \gamma].$$

Hence, if we rewrite Eq. (44) in the form

$$[\hat{\varepsilon}(\gamma), \gamma] = i(\partial \gamma / \partial t - L^{(2)}(\gamma)), \quad (51)$$

we get in zeroth approximation the equation:

$$[\hat{\varepsilon}(\gamma), \gamma] = 0.$$

The matrix (47) is the solution of this equation. In the next approximation Eq. (51) for the small correction $\gamma^{(1)}$ to the matrix (47) looks like:

$$[\hat{\varepsilon}, \gamma^{(1)}] + [\hat{\varepsilon}^{(1)}, \gamma] = i(\partial \gamma / \partial t - L^{(2)}(\gamma)).$$

From the condition that this equation is solvable we get

$$\text{Sp}_r \left(E_{\lambda} \frac{\partial \gamma}{\partial t} \right) = \text{Sp}_r (E_{\lambda} L^{(2)}(\gamma)),$$

or, by virtue of Eqs. (47) and (48), alternatively

$$\partial \varphi_{\lambda} / \partial t = I_{\lambda} \{ \varphi \}, \quad I_{\lambda} \{ \varphi \} = \text{Sp}_r (E_{\lambda} L^{(2)}(\gamma)). \quad (52)$$

Using Eqs. (38), (8), (9), (22), (45), (47), and (48) we can find the explicit form of the collision integral $I_{\lambda} \{ \varphi \}$ of (52). First of all, since the matrix γ in the form (47) is a "stationary point" of Eq. (46), we may assume in Eq. (22) that $\mathcal{H}_S(S_{\tau}^{(0)}(\gamma)) = \mathcal{H}_S(\gamma) = \text{const}$ for the operator $U(\tau, 0; \gamma)$, since according to the definition (20) in that case $S_{\tau}^{(0)}(\gamma) = \gamma$. Hence it follows that

$$U(\tau, 0; \gamma) = \exp(-i\mathcal{H}_S \tau). \quad (53)$$

We expand the operators $\varphi(\mathbf{r})$ and $\varphi^+(\mathbf{r})$ in terms of the single-particle states $|\mathbf{r}, \lambda\rangle$ of (49):

$$\varphi(\mathbf{r}) = \sum_{\lambda} b_{\lambda} |\mathbf{r}, \lambda\rangle, \quad \varphi^+(\mathbf{r}) = \sum_{\lambda} \langle \mathbf{r}, \lambda | b_{\lambda}^{\dagger}. \quad (54)$$

One sees easily from Eqs. (8), (47), and (48) that the distribution function φ_{λ} is equal to

$$\varphi_{\lambda} = \langle b_{\lambda} b_{\lambda}^{\dagger} \rangle, \quad \text{Sp}_r (E_{\lambda} \hat{\gamma}) = b_{\lambda} b_{\lambda}^{\dagger}. \quad (55)$$

Substituting expansion (54) into Eqs. (9) and (45) we get

$$\mathcal{H}_s = \sum_{\lambda} \varepsilon_{\lambda} b_{\lambda}^{\dagger} b_{\lambda},$$

$$\mathcal{H}_{int} = \sum_{\lambda_1 \lambda_2 \lambda_3 \lambda_4} M_{\lambda_1 \lambda_2; \lambda_3 \lambda_4} b_{\lambda_1}^{\dagger} b_{\lambda_2} b_{\lambda_3}^{\dagger} b_{\lambda_4}, \quad (56)$$

where $M_{\lambda_1 \lambda_2; \lambda_3 \lambda_4}$ is the matrix element of the interaction:

$$M_{\lambda_1 \lambda_2; \lambda_3 \lambda_4} = g \int dV \langle \lambda_1, \mathbf{r} | \sigma_x | \mathbf{r}, \lambda_2 \rangle \langle \lambda_3, \mathbf{r} | \sigma_y | \mathbf{r}, \lambda_4 \rangle. \quad (57)$$

Substitution of Eqs. (53), (55), and (56) into Eq. (38) gives the following result for the collision integral $I_{\lambda} \{ \varphi \}$ of (52):

$$I_{\lambda} \{ \varphi \} = - \int_{-\infty}^0 d\tau e^{\eta \tau} \langle [\mathcal{H}_{int}(\tau), [\mathcal{H}_{int}(\tau), b_{\lambda} b_{\lambda}^{\dagger}]] \rangle, \quad \eta \rightarrow +0, \quad (58)$$

where $\mathcal{H}_{int}(\tau)$ differs from \mathcal{H}_{int} by the replacement of the matrix element $M_{\lambda_1 \lambda_2; \lambda_3 \lambda_4}$ by

$$M_{\lambda_1 \lambda_2; \lambda_3 \lambda_4}(\tau) = M_{\lambda_1, \lambda_2; \lambda_3 \lambda_4} \exp [i(\varepsilon_{\lambda_1} + \varepsilon_{\lambda_2} - \varepsilon_{\lambda_3} - \varepsilon_{\lambda_4})\tau].$$

The remaining calculations in Eq. (58) reduce to the standard calculation of commutators and the subsequent averaging using Wick's theorem. The final result for the collision integral looks as follows:

⁵⁾Equations analogous to (46) and (43) written down for correlation functions were used in [12] to derive the equations for the two-fluid hydrodynamics of a superfluid Fermi-gas (see also [13, 14]).

$$I_{\lambda}(\varphi) = \sum_{\lambda_1, \lambda_2, \lambda_3, \lambda_4} \pi \delta(\epsilon_{\lambda_1} + \epsilon_{\lambda_2} - \epsilon_{\lambda_3} - \epsilon_{\lambda_4}) |M_{\lambda_1, \lambda_2; \lambda_3, \lambda_4} - M_{\lambda_1; \lambda_2, \lambda_3} + M_{\lambda_1, \lambda_3; \lambda_2, \lambda_4} - M_{\lambda_1, \lambda_4; \lambda_2, \lambda_3}|^2 [(1 - \varphi_{\lambda_1})(1 - \varphi_{\lambda_2})\varphi_{\lambda_3}\varphi_{\lambda_4} - \varphi_{\lambda_1}\varphi_{\lambda_2}(1 - \varphi_{\lambda_3})(1 - \varphi_{\lambda_4})]. \quad (59)$$

By virtue of the definition (8) of the matrix γ , the equilibrium distribution function determined by this collision integral ($\partial\varphi_{\lambda}/\partial t = 0$) is clearly equal to

$$\varphi_{\lambda} = 1 - f(\epsilon_{\lambda}/T), \quad f(x) = (e^x + 1)^{-1}. \quad (60)$$

We must then note that because of the used definition (7) of electrons and holes the constant correction to the energy ϵ_{λ} in Eq. (60) postulated by the integral (59) would determine a separation of the Fermi surfaces for electrons with opposite spins. The true chemical potential connected with the conservation of the number of electrons (see Eq. (44)) is contained in the phase of the ordering parameter χ and in the equilibrium state we see from Eq. (42) that we have $\partial\chi/\partial t \approx 2\mu$ apart from a small renormalization.

It follows from Eqs. (47), (48), and (60) that the equilibrium density matrix is equal to

$$\gamma = 1 - f(\hat{\epsilon}/T). \quad (61)$$

Using the expansion

$$1 - f\left(\frac{\hat{\epsilon}}{T}\right) = T \sum_n \frac{\exp\{-i\omega_n \eta\}}{\hat{\epsilon} - i\omega_n}, \quad \eta \rightarrow +0, \\ \omega_n = \pi T(2n + 1), \quad n = 0, \pm 1, \pm 2, \dots,$$

we see easily that the equilibrium density matrix (61) which we have found is determined in terms of the temperature-dependent Green function:

$$\gamma = G(\tau + 0, \tau), \quad (\partial/\partial\tau_1 + \hat{\epsilon})G(\tau_1, \tau_2) = \delta(\tau_1 - \tau_2). \quad (62)$$

Using the definition (42) we can verify that Eq. (62) together with the self-consistency equations (43) and (44) is equivalent to Gor'kov's equations^[5, 9] in matrix notation.

In connection with the fact that the matrix γ is non-diagonal in the "isotopic spin" in the electron-hole space it is of interest to study in more detail the relaxation process leading to the formation of the superconducting condensate, i.e., to the appearance of the self-consistent field of the parameter Δ and the quasiparticle description of the excitations. In its pure form this process appears when there are no external fields in the spatially uniform case, when

$$\gamma(r_1, r_2) = \frac{1}{V} \sum_p \gamma_p \exp[ip(r_1 - r_2)],$$

where V is the normalization volume while Eqs. (42) to (45) take the form

$$i\partial\gamma_p/\partial t = [\hat{\epsilon}_p, \gamma_p], \quad (63) \\ \hat{\epsilon}_p = \sigma_z \xi_p + \sigma_x \Delta, \quad \xi_p = \mathcal{E}(p) - \mu, \\ \mu = -\frac{1}{2} \left(\frac{\partial\chi}{\partial t} + gn \right), \quad \frac{1}{2} n = n_{\uparrow} = n_{\downarrow} = \text{const}; \\ \Delta = \frac{|g|}{2V} \sum_p \text{Tr}(\sigma_z \gamma_p), \quad 0 = \frac{|g|}{2V} \sum_p \text{Tr}(\sigma_y \gamma_p). \quad (64)$$

The function ξ_p in (63) is clearly of the same order of magnitude as the electron energy reckoned from the Fermi boundary.

For what follows it is sufficient to consider the asymptotic behavior of the solutions of Eqs. (63) and (64) as $t \rightarrow \infty$. In that way we shall study the relaxation process described by these equations. The following relations for the derivatives $\partial\Delta/\partial t$ and $\partial\mu/\partial t$ follow from Eqs. (63) and (64):

$$\frac{\partial\Delta}{\partial t} = -\frac{|g|}{V} \sum_p \xi_p \text{Tr}(\sigma_y \gamma_p), \quad \frac{\partial\mu}{\partial t} = -\frac{1}{2} \frac{\partial^2\chi}{\partial t^2}, \\ \Delta \frac{\partial\mu}{\partial t} = -\frac{|g|}{V} \sum_p \xi_p \mathcal{E}(p) \text{Tr}(\sigma_y \gamma_p). \quad (65)$$

Hence we can see that as $t \rightarrow \infty$ we have $\partial\Delta/\partial t \rightarrow 0$, $\partial\mu/\partial t \rightarrow 0$, and hence (see Eq. (63)) $\hat{\epsilon}_p \rightarrow \text{const}$. Indeed, it follows in that case from Eq. (63) that

$$t \rightarrow \infty, \quad \gamma_p \rightarrow \exp(-i\hat{\epsilon}_p t) \beta_p \exp(i\hat{\epsilon}_p t), \quad (66)$$

where β_p is a constant matrix.

Introducing the projection operators constituting the expansion of unity for the Hermitian matrix $\hat{\epsilon}_p$ of (63):

$$E_{p\sigma} = 1/2(1 + \sigma\hat{\epsilon}_p/\epsilon_p) \quad (\sigma = \pm 1), \quad \hat{\epsilon}_p = \sum_{\sigma} \sigma E_{p\sigma} E_{p\sigma}, \quad (67)$$

$$\hat{\epsilon}_p^2 = \epsilon_p^2, \quad \epsilon_p = \sqrt{\xi_p^2 + \Delta^2}, \quad E_{p\sigma} E_{p\sigma'} = \delta_{\sigma\sigma'} E_{p\sigma}, \quad \sum_{\sigma} E_{p\sigma} = 1,$$

we write Eq. (66) in the following form:

$$t \rightarrow \infty, \quad \gamma_p \rightarrow \sum_{\sigma, \sigma'} E_{p\sigma} \beta_p E_{p\sigma'} \exp[-i(\sigma - \sigma')\epsilon_p t]. \quad (68)$$

Substituting this last expression into Eqs. (65) we obtain

$$\frac{\partial\Delta}{\partial t} \rightarrow -\frac{|g|}{V} \sum_{p, \sigma} \xi_p \text{Tr}(\sigma_y E_{p\sigma} \beta_p E_{p\sigma}) - \\ - \frac{|g|}{V} \sum_{p, \sigma} \xi_p \text{Tr}(\sigma_y E_{p\sigma} \beta_p E_{p, -\sigma}) \exp(-2i\sigma\epsilon_p t).$$

The last term in this equation vanishes as $t \rightarrow \infty$ owing to the fast oscillations of the function under the summation sign. Using Eqs. (67) and (63) we have thus

$$\frac{\partial\Delta}{\partial t} \rightarrow -\frac{|g|}{V} \sum_{p, \sigma} \xi_p \text{Tr}(\sigma_y E_{p\sigma} \beta_p E_{p\sigma}) = -\frac{|g|}{V} \sum_{p, \sigma} \xi_p \text{Tr}(\sigma_y E_{p\sigma}) \text{Tr}(\beta_p E_{p\sigma}) = 0.$$

The equation $\partial\mu/\partial t = 0$ is proved analogously.

The equations obtained are clearly a consequence of the fact that the ordering parameter Δ is a self-averaging quantity. We showed that all physical quantities can be expressed in terms of some sums of the matrices γ_p over p . After the lapse of a sufficiently long time $t \gg \tau_1 \sim 1/T_c$ the oscillating terms in Eq. (68) for the matrix γ_p therefore do not contribute to these quantities and the matrix γ_p is asymptotically equivalent to the following one (compare Eq. (47)):

$$\gamma_p = \sum_{\sigma} \varphi_{p\sigma} E_{p\sigma}, \quad \varphi_{p\sigma} = \text{Tr}(E_{p\sigma} \beta_p). \quad (69)$$

Substituting Eqs. (69) and (67) into Eq. (64) which determines the quantity Δ , we get for it the following asymptotic equation (in the limit as $V \rightarrow \infty$):

$$\Delta = |g| \int \frac{d^3p}{(2\pi)^3} \frac{\Delta}{2\epsilon_p} \sum_{\sigma} \sigma \varphi_{p\sigma}, \quad (70)$$

i.e., the BCS equation^[1] with a non-equilibrium distribution function.

Using Equations (67) we can evaluate the matrix element (57) in the collision integral (59) and find the equation determining the slow change in the distribution function $\varphi_{\mathbf{p}\sigma}$:

$$\begin{aligned} \frac{\partial \varphi_{\mathbf{p}\sigma}}{\partial t} = & \frac{g^2}{(2\pi)^3} \sum_{\sigma_1, \sigma_2} \iiint d^3\mathbf{p}_2 d^3\mathbf{p}_3 d^3\mathbf{p}_4 \delta(\mathbf{p} + \mathbf{p}_2 - \mathbf{p}_3 - \mathbf{p}_4) \delta(\sigma_1 \sigma_2) \\ & + \sigma_2 \varepsilon_{\mathbf{p}_2} - \sigma_3 \varepsilon_{\mathbf{p}_3} - \sigma_4 \varepsilon_{\mathbf{p}_4} \frac{1}{8} \left(1 - \sigma \sigma_2 \frac{\xi_{\mathbf{p}} \xi_{\mathbf{p}_2} + \Delta^2}{\varepsilon_{\mathbf{p}} \varepsilon_{\mathbf{p}_2}} \right) \left(1 - \sigma_3 \sigma_4 \frac{\xi_{\mathbf{p}_3} \xi_{\mathbf{p}_4} + \Delta^2}{\varepsilon_{\mathbf{p}_3} \varepsilon_{\mathbf{p}_4}} \right) \left[(1 - \varphi_{\mathbf{p}\sigma}) (1 - \varphi_{\mathbf{p}_2 \sigma_2}) \varphi_{\mathbf{p}_3 \sigma_3} \varphi_{\mathbf{p}_4 \sigma_4} \right. \\ & \left. - \varphi_{\mathbf{p}\sigma} \varphi_{\mathbf{p}_2 \sigma_2} (1 - \varphi_{\mathbf{p}_3 \sigma_3}) (1 - \varphi_{\mathbf{p}_4 \sigma_4}) \right]; \\ \varepsilon_{\mathbf{p}} = & \sqrt{\xi_{\mathbf{p}}^2 + \Delta^2}, \quad \xi_{\mathbf{p}} = \mathcal{E}(\mathbf{p}) - \mu = p^2/2m - \mu. \quad (71) \end{aligned}$$

We must emphasize that notwithstanding the formal agreement of this equation with the usual kinetic equation for normal excitations in a metal (with a dispersion law $\varepsilon_{\mathbf{p}} = \sqrt{(\xi_{\mathbf{p}}^2 + \Delta^2)}$) it nevertheless differs appreciably from the latter since Eq. (71) contains self-consistent parameter Δ , which depends on the instantaneous distribution function $\varphi_{\mathbf{p}\sigma}$ through Eq. (70) and which relaxes together with that function.

We must add to Eqs. (71) and (70) the second equation (64) which determines the parameter μ (the instantaneous value of the chemical potential) and the rate of change in the phase χ of the ordering parameter. One sees easily that in zeroth approximation of (69) this equation is satisfied identically since it contains the conservation law for the particle number in the system, i.e., in the given case the relation $\partial n / \partial t = 0$, which is a relation of first order in the velocity of change of the quantities $\varphi_{\mathbf{p}\sigma}$, Δ , and μ . The latter can be verified by direct calculation, starting from the correction in the first approximation $\gamma^{(1)}$ from Eq. (51) and substituting it into Eq. (64):

$$\frac{|g|}{2V} \sum_{\mathbf{p}} \text{Tr}(\sigma_y \gamma_{\mathbf{p}}^{(1)}) = 0.$$

The complete set of equations determining the evolution of the distribution functions $\varphi_{\mathbf{p}\sigma}$ and of the parameters Δ and μ contains thus, apart from Eqs. (70) and (71), also the condition that the number of particles be constant:

$$n = \int \frac{d^3\mathbf{p}}{(2\pi)^3} \sum_{\sigma} \left(\frac{1}{2} - \frac{\xi_{\mathbf{p}}}{\varepsilon_{\mathbf{p}}} \sigma \varphi_{\mathbf{p}\sigma} \right) = \text{const.}$$

The characteristic time during which the equilibrium state is reached is, as simple estimates in the collision integral of (71) show, as to order of magnitude, equal to

$$\tau_2 \sim \left[(g m p_F)^2 T_c \frac{T_c}{\mu} \right]^{-1} \sim 10^{-8} \text{ cек} \left(\frac{p_F^2}{2m} = \mu \right),$$

i.e., it does not differ from the electron relaxation time in the normal metal at the same temperatures.

The self-consistent Eq. (70) possesses a specific singularity: together with a possible non-trivial solution $\Delta \neq 0$ it always has the trivial solution $\Delta = 0$ describing the normal state. In this connection the problem of the choice of the solution of that equation may arise, for instance, for a given initial distribution $\varphi_{\mathbf{p}\sigma}$. In reality the choice of solution is realized automatically after the lapse of a time τ_1 in correspondence with the initial conditions for the matrix $\gamma_{\mathbf{p}}$ in Eqs. (63). However, only the problem of the stability of this or that solution has a physical meaning and in that sense

Eq. (63) is remarkable because it describes the well-known Cooper instability^[15] of the normal state for temperatures $T < T_c$. Indeed, in the equilibrium normal state the matrix $\gamma_{\mathbf{p}}$ has according to (61) and (63) the following form:

$$\gamma_{\mathbf{p}} = \frac{1}{2} \left(1 + \sigma_x \text{th} \frac{\xi_{\mathbf{p}}}{2T} \right).$$

Considering a small perturbation $\delta\gamma_{\mathbf{p}}$ destroying the diagonality of this matrix ($\text{Tr} \delta\gamma_{\mathbf{p}} = \text{Tr}(\sigma_z \delta\gamma_{\mathbf{p}}) = 0$), we get from (63) a linear equation for $\delta\gamma_{\mathbf{p}}$:

$$i \frac{\partial}{\partial t} \delta\gamma_{\mathbf{p}} = \xi_{\mathbf{p}} [\sigma_x, \delta\gamma_{\mathbf{p}}] - \frac{1}{2} \text{th} \frac{\xi_{\mathbf{p}}}{2T} \left[\sigma_x, \frac{|g|}{V} \sum_{\mathbf{p}'} \delta\gamma_{\mathbf{p}'} \right].$$

The solution of this equation through a Laplace transformation leads to the following expression:

$$\delta\gamma_{\mathbf{p}} = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} d\omega e^{i\omega t} (i\omega - 2\sigma_x \xi_{\mathbf{p}})^{-1} \left(\delta\gamma_{\mathbf{p}}(0) - \text{th} \frac{\xi_{\mathbf{p}}}{2T} \sigma_x \delta w(\omega) \right), \quad (72)$$

where $\delta\gamma_{\mathbf{p}}(0)$ is the initial value of the perturbation while the quantity $\delta w(\omega)$ has the form

$$\delta w(\omega) = \frac{i|g|}{V} \sum_{\mathbf{p}} (i\omega - 2\sigma_x \xi_{\mathbf{p}})^{-1} \delta\gamma_{\mathbf{p}}(0) \left[1 - \frac{|g|}{V} \sum_{\mathbf{p}'} \frac{2\xi_{\mathbf{p}'}}{\omega^2 + 4\xi_{\mathbf{p}'^2}} \text{th} \frac{\xi_{\mathbf{p}'}}{2T} \right]^{-1}. \quad (73)$$

One sees easily that the real positive pole of the function $\delta w(\omega)$ determines the exponentially increasing solution for $\delta\gamma_{\mathbf{p}}$ of (72) ($\delta\gamma_{\mathbf{p}} \sim \exp \omega_0 t$). After the usual transformations involving replacing the integration over momenta by an integration over the energy near the Fermi surface and using the definition of the critical temperature T_c ^[1] the equation for ω_0 takes the form:

$$\int_0^{\infty} d\xi \frac{\text{th}(\xi/2T)}{\xi} \frac{\omega_0^2}{\omega_0^2 + 4\xi^2} = \ln \frac{T_c}{T}.$$

The real root of this equation occurs when $T < T_c$. We have then asymptotically

$$T \rightarrow T_c - 0, \quad \omega_0 \approx \frac{8(T_c - T)}{\pi}; \quad T \rightarrow 0, \quad \omega_0 \approx \frac{2\pi T_c}{V} = 2\Delta(0),$$

where $\ln \gamma = C = 0.577$ and $2\Delta(0)$ is the BCS gap^[1] in the superconductor energy spectrum at $T = 0$.

The kinetic equations for the generalized electron density matrix of a superconductor considered in the present paper enable us to evaluate various non-stationary processes in superconductors. In particular, using perturbation theory we can find the linear responses, for instance, to a weak electric field. One can show that the corresponding results in that case are the same as the well-known ones.^[3, 5] These equations enable us moreover to study the problem of the time-dependent Ginzburg-Landau equations,^[16] the viscous transfer coefficients in the hydrodynamic equations of a superfluid Fermi gas, and also to investigate different non-linear effects in superconductors. We hope to consider a number of such problems in the near future.

The author is grateful to S. V. Peletminskii for discussions of this paper.

¹J. Bardeen, L. Cooper, and J. Schrieffer, Phys. Rev. 108, 1175 (1957).

²N. N. Bogolyubov, V. V. Tolmachev, and D. V. Shirkov, Novyi metod v teorii sverkhprovodimosti (A New Method in the Theory of Superconductivity), Izd. Akad.

Nauk SSSR, 1958 [Engl. translation published by Consultants Bureau].

³A. A. Abrikosov, L. P. Gor'kov, and I. M. Khalatnikov, *Zh. Eksp. Teor. Fiz.* **35**, 265 (1958) [*Sov. Phys.-JETP* **8**, 182 (1959)].

⁴R. Kubo, *J. Phys. Soc. Japan* **12**, 570 (1957).

⁵A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskii, *Metody kvantovoi teorii polya v statisticheskoi fizike* (Quantum Field Theoretical Methods in Statistical Physics), Fizmatgiz, 1962 [English translation published by Pergamon Press, Oxford, 1965].

⁶B. D. Josephson, *Rev. Mod. Phys.* **36**, 221 (1964).

⁷Y. B. Kim, C. F. Hempstead, and A. R. Strnad, *Phys. Rev.* **139**, A1163 (1965).

⁸L. P. Gor'kov and G. M. Éliashberg, *Zh. Eksp. Teor. Fiz.* **54**, 612 (1968) [*Sov. Phys.-JETP* **27**, 328 (1968)].

⁹L. P. Gor'kov, *Zh. Eksp. Teor. Fiz.* **34**, 735 (1958) [*Sov. Phys.-JETP* **7**, 505 (1958)].

¹⁰N. N. Bogolyubov, *Problemy dinamicheskoi teorii v statisticheskoi fizike* (Problems of the Dynamical

Theory in Statistical Physics), Gostekhizdat, 1946 [English translation published in *Studies in Statistical Mechanics*, North Holland, Amsterdam].

¹¹S. V. Peletminskii and A. A. Yatsenko, *Zh. Eksp. Teor. Fiz.* **53**, 1327 (1967) [*Sov. Phys.-JETP* **26**, 773 (1968)].

¹²M. J. Stephen, *Phys. Rev.* **139**, A197 (1965).

¹³M. P. Kemoklidze and L. P. Pitaevskii, *Zh. Eksp. Teor. Fiz.* **50**, 243 (1966) [*Sov. Phys.-JETP* **23**, 160 (1966)].

¹⁴A. V. Svidzinskii and V. A. Slyusarev, *Gyrodinamicheskie uravneniya v mikroskopicheskoi teorii sverkhprovodimosti* (Hydrodynamic Equations in the Microscopic Theory of Superconductivity), Preprint, VINITI, 1965.

¹⁵L. N. Cooper, *Phys. Rev.* **104**, 1189 (1957).

¹⁶A. Abrahams and T. Tsuneto, *Phys. Rev.* **152**, 416 (1966).

Translated by D. ter Haar