

# The formation of the order parameter in BCS model near $T_c$

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The classical selfconsistency equation used in most papers is valid if the formation time of the pair condensate is much shorter than the other characteristic times. This assumption is not valid in the problem of the emergence of the superconducting state. In a number of works the kinetic properties are considered using the reduced hamiltonian of BCS model and the electron-electron collisions are completely disregarded. However we emphasize that the superconducting pairing of electrons is a small effect against the background of stronger interaction in the electronic Fermi liquid of the metal. In this work, we assume that collisions between excitations are sufficiently frequent and lead to the thermalization of excitations, whereas the order parameter varies quite slowly. In the present work the physical picture for the emergence of the superconducting state is considered in a supercooled electron gas.

Assuming a slow rate for the phase transition it is possible to construct approximately stationary states with the superconductive nuclei of finite size. It's evolution rate is defined by the collisions of excitations changing the number of electrons in Cooper pairs. The problem of the uniform relaxation of the order parameter along this lines was considered by Lordanskiy, Saptsov, Brener (2007) in [8] .

The main difficulty in the construction of the quasistationary states is the impossibility to satisfy the selfconsistency equation for the equilibrium distribution of quasiparticles. The physical base for the consideration of quasistationary states with the nonequilibrium values of the order parameter is given by Landau assumption of the large relaxation time in the vicinity of the critical temperature. It is possible to consider the states with the nonequilibrium values of the order parameter as approximately stationary states using Lagrange method to find the minima of BCS hamiltonian at given modulo square of the order parameter.

The original BCS hamiltonian has the form

$$H_{bcs}^0 = \int d^3r [\psi_{\sigma}^+(\mathbf{r})(\hat{\epsilon}_0 - \mu)\psi_{\sigma}(\mathbf{r}) - \lambda_0 \psi_{+}^+(\mathbf{r})\psi_{-}^+(\mathbf{r})\psi_{-}(\mathbf{r})\psi_{+}(\mathbf{r})] \quad (1)$$

where  $\epsilon_0 = (i\hbar)^2/(2m)(\nabla)^2$ ,  $\mu = (p_F)^2/2m$  is the electron chemical potential,  $\sigma = (+), (-)$  are spin indices,  $\lambda_0$  is the interaction constant.

Assuming a given value of  $|\Phi(\mathbf{r})|^2$  we introduce the proper Lagrange multiplier  $\delta\lambda(\mathbf{r})$  and a new effective hamiltonian

$$H'_{bcs} = H_{bcs}^0 - \int d^3r \delta\lambda(\mathbf{r}) \psi_+^+(\mathbf{r}) \psi_-^+(\mathbf{r}) \psi_-(\mathbf{r}) \psi_+(\mathbf{r}) \quad (2)$$

That is equivalent to the considering of BCS model with the changing in space interaction constant  $\lambda_{eff}(\mathbf{r})$ . It is possible to treat the effective hamiltonian (2) by the standard mean field theory trying to find stationary states close to  $T_c$ . Following [9] one can use the perturbation theory in  $\Delta$  for Gorkov Matsubara functions

$$\begin{aligned} G_{\alpha\beta}(\mathbf{r}, \tau; \mathbf{r}', \tau') &= - \langle T_\tau \psi_\alpha^+(\mathbf{r}', \tau') \psi_\beta(\mathbf{r}, \tau) \rangle \\ F_{\alpha\beta}(\mathbf{r}', \tau'; \mathbf{r}, \tau) &= g_{\alpha\beta} \langle T_\tau \psi_\alpha(\mathbf{r}', \tau') \psi_\beta(\mathbf{r}, \tau) \rangle \end{aligned} \quad (3)$$

The equations for the Green contain the gap function defined by the selfconsistency equation

$$\Delta(\mathbf{r}) = \lambda_{\text{eff}}(\mathbf{r})F(\mathbf{r}, \tau' = \tau + 0, \mathbf{r}, \tau) \quad (4)$$

It is essential that the Green functions are periodic in  $\tau$  and are unambiguously defined by the equations for their Fourier components

$$i\omega_n G_{\omega_n}(\mathbf{r}, \mathbf{r}') = (\hat{\epsilon}_0(\mathbf{r}) - \mu) G_{\omega_n}(\mathbf{r}, \mathbf{r}') + \Delta(\mathbf{r}) F_{\omega_n}^+(\mathbf{r}, \mathbf{r}') \quad (5)$$

$$i\omega_n F_{\omega_n}^+(\mathbf{r}, \mathbf{r}') = -(\hat{\epsilon}_0(\mathbf{r}) - \mu) F_{\omega_n}^+(\mathbf{r}, \mathbf{r}') + \Delta^* G_{\omega_n}(\mathbf{r}, \mathbf{r}') \quad (6)$$

and depend only on the gap function  $\Delta$ . Really we need the expansion of  $F_{\omega_n}^+$  near  $T_c$  up to

$$\begin{aligned}
 F_{\omega_n}^+(\mathbf{r}, \mathbf{r}') &= \int d^3s G_{\omega_n}^0(\mathbf{r}, \mathbf{s}) \Delta^*(\mathbf{s}) G_{\omega_n}^0(\mathbf{s}, \mathbf{r}') - \\
 &\int d^3s d^3s' d^3s'' G_{-\omega_n}^0(\mathbf{r}, \mathbf{s}) \Delta^*(\mathbf{s}) G_{\omega_n}^0(\mathbf{s}, \mathbf{s}') \Delta(\mathbf{s}') \\
 &\quad G_{-\omega_n}^0(\mathbf{s}', \mathbf{s}'') \Delta^*(\mathbf{s}'') G_{\omega_n}^0(\mathbf{s}'', \mathbf{r}')
 \end{aligned} \tag{7}$$

Here  $G^0$  is the corresponding Green function for the noninteracting electron gas

$$G_{\omega_n}^0(\mathbf{r}, \mathbf{r}') = -\frac{m}{2\pi R} \exp \left[ \left( ip_F \operatorname{sign} \omega_n - \frac{|\omega_n|}{v_F} \right) R \right] \tag{8}$$

where  $R = |\mathbf{r} - \mathbf{r}'|$ .

The expression for the modified BCS energy(2) can be also expressed in terms of  $\Delta$

$$\begin{aligned} \langle H'_{BCS} \rangle = & 2 \int d^3r (\hat{\epsilon}_0(\mathbf{r} - \mu) G(\mathbf{r}, \tau; \mathbf{r}', \tau') |_{(\tau' \rightarrow \tau + 0, \mathbf{r} \rightarrow \mathbf{r}')} \quad (9) \\ & - \int d^3r \Delta(\mathbf{r}) F^+(\mathbf{r}, \mathbf{r}'; \tau, \tau') |_{(\tau \rightarrow \tau' + 0), (\mathbf{r} \rightarrow \mathbf{r}')} \end{aligned}$$

We can use the first equation (5) for  $G$  to exclude differentiation in the first term of (9). Thus we obtain more convenient expression for the thermodynamic energy

$$\begin{aligned} \langle H'_{bcs} \rangle = & -3 \int d^3r \Delta(\mathbf{r}) F^+(\mathbf{r}, \mathbf{r}, \tau \rightarrow \tau' + 0) \\ & + 2T \sum_n \delta G_{\omega_n}(\mathbf{r}, \mathbf{r}; \tau \rightarrow \tau' + 0) \end{aligned} \quad (10)$$

here

$$\delta G_{\omega_n} = \int d^3s G_{\omega_n}^0(\mathbf{r}, \mathbf{s}) \Delta(\mathbf{s}) F_{\omega_n}^+(\mathbf{s}, \mathbf{r})$$

Because Green function (8) strongly oscillates on the distances of the order of  $v_F/T \gg \frac{\hbar}{p_F}$  therefore it is possible to neglect the last term as a small quantity of the order of  $T/\mu$  compare to the first. Using expansion (7) it is possible to calculate the expansion in  $\Delta$  for the thermodynamic energy of quasistationary states.

We assume that the gap function has a small change on the distances of the order of  $\xi_0 = v_F/T$  and the gradient energy is small. In the vicinity of  $T_c$  the gap is always small and the non local corrections are essential only for quadratic terms in energy neglecting such corrections for the quartic terms, which can be computed in the local approximation.

The quadratic terms in BCS thermodynamic energy (10) has the form

$$H'_{bcs}^{(2)} = -3 \int d^3r d^3s |\Delta|^2(\mathbf{r}) T \sum_n G_{-\omega_n}^0(\mathbf{r}, \mathbf{s}) G_{\omega_n}^0(\mathbf{s}, \mathbf{r}) - \quad (11)$$

$$3 \int d^3r d^3s \Delta^*(\mathbf{r}) \frac{1}{2} \frac{\partial^2 \Delta}{\partial r_i \partial r_k} (r_i - s_i)(r_k - s_k) G_{-\omega_n}^0(\mathbf{r}, \mathbf{s}) G_{\omega_n}^0(\mathbf{s}, \mathbf{r})$$

Linear in derivatives terms vanish due to isotropy. The sum in the first term has a logarithmic divergence. Really we can use the known results from [9] for all terms in thermodynamic BCS energy up to quartic in  $\Delta$

$$H'_{bcs} = -\frac{3mp_F}{2\pi^2} \left[ \ln \frac{2\gamma\omega_D}{\pi T} \right] \int d^3r |\Delta(\mathbf{r})|^2 + \quad (12)$$

$$\frac{21\zeta(3)mp_F v_F^2}{32\pi^4 T^2} \int d^3r |\Delta(\mathbf{r})|^4 - \frac{7\zeta(3)mp_F v_F^2}{4\pi^4 T^2} \int d^3r \Delta^* \frac{\partial^2 \Delta}{\partial r_k^2}$$

Here  $\gamma$  is the Euler constant,  $\zeta(3)$  is the zeta Riemann function,  $\omega_D$  is the Debay energy.

This expression has the standard form of Ginsburg-Landau free energy giving the possibility to find stationary states with a definite number of electrons in Cooper pairs proportional to

$$\nu = \int d^3r |\Delta(\mathbf{r})|^2 \quad (13)$$

minimizing the new thermodynamic potential

$$\Omega(\Delta) = H'_{bcS}(\Delta) - \Lambda \int d^3r |\Delta(\mathbf{r})|^2 \quad (14)$$

with Lagrange multiplier  $\Lambda$ . Therefore the stationary states with a definite number  $\nu$  with  $\Delta \neq 0$  in a finite volume of electron gas are defined by a kind of nonlinear Schroedinger equation

$$\frac{\delta H'_{bcS}}{\delta \Delta^*} - \Lambda \Delta = 0 \quad (15)$$

The value of  $\Delta$  can not be smaller than the quantum energetic correction due to the relaxation process  $\Delta > \hbar/\tau_r$ . At smaller values a rapid relaxation of  $\Delta$  to zero occurred by the fluctuations destroying the coherence of the order parameter. Therefore the equation (??) is valid only at  $|\Delta| > \Delta_1$  where  $\Delta_1$  is some phenomenological constant. Because of the rapid change of  $\Delta$  in space at the smaller values there is some surface tension  $\sigma(\Delta_1)$  which must be taken into account in the stability condition for the solutions of (??) . Assuming the spherical symmetry of the superconducting nuclei it is possible to obtain a kind of Laplace formulae at its boundary  $r = R$  by the the variation of (14) in  $R$

$$\alpha \left| \frac{\partial \Delta}{\partial r} \right|^2 - \beta |\Delta_1|^2 + \frac{2\sigma(\Delta_1)}{R} = 0 \quad (16)$$

Here the first two terms are defined by the  $\Delta$  expansion in (14). Two boundary conditions (16) and  $\Delta = \Delta_1$  and the equation (??) determine  $R(\Lambda)$ ,  $\Delta(\Lambda, r)$  assuming given small value of  $\Delta_1$ . Thus we have a family of solutions depending on one real parameter  $\Lambda$ .

The convenient parametrization of the obtained family of quasistationary states is given by the electron number in Cooper pairs of the superconducting nuclei. In the absence of the processes changing this number these states can be considered as stationary. For the description of the relaxation process one needs to find the connection of the electron number in Cooper pairs  $N_s$  with the normalization constant  $\nu$  in(13).

Assuming the large scale for the variation of  $\Delta$  in the superconducting nuclei it is possible to neglect the nonlocal corrections and obtain the electron density by Bogolyubov transformation in the form

$$n_e = 2 \int \frac{d^3 p}{2\pi^3} v_p^2 + 2 \int \frac{d^3 p}{2\pi^3} (u_p^2 - v_p^2) n(\mathbf{p}, \mathbf{r}) \quad (17)$$

where the coherence factors  $u_p(\mathbf{r}), v_p(\mathbf{r})$  are defined by the standard formulae

$$u_p^2 + v_p^2 = 1, \quad u_p^2 - v_p^2 = \eta_p / \epsilon(p)$$

where  $\eta_p = p^2 / 2m - \mu$ , excitation energy  $\epsilon(p) = \sqrt{|\Delta|^2 + \eta(p)^2}$  and  $n(\mathbf{p}, \mathbf{r})$  is the distribution function of excitations.

The first term in (17) is the number density of electrons in Cooper pairs whereas the second term gives the electron number in excitations.

The electron density in Cooper pairs is proportional to  $|\Delta|^2$  with the proportionality coefficient found in ([8])  $n_s = mp_F/\pi^2\hbar T_c|\Delta|^2$ . The total number of electrons in Cooper pairs of the superconducting nuclei is

$$N_s = \frac{mp_F}{\pi^2\hbar^3 T_c} \int d^3r |\Delta|^2 \quad (18)$$

This quantity can be changed by the processes of the annihilation of two excitations or by the scattering of excitations both with the phonon emission. The phonon is needed to take or supply the extra energy. We do not consider the processes of triple excitation collisions.

The total energy of the quasistationary states for the superconducting nuclei is given by the original BCS Hamiltonian (1) with the interaction constant  $\lambda_0$  and can be expressed in the terms of the Matsubara Green functions as

$$\langle H_{bcs}^0 \rangle = \int d^3r (\hat{\epsilon}_r^0 - \mu) G(\mathbf{r}, \tau; \mathbf{r}', \tau + 0)|_{\mathbf{r}'=\mathbf{r}} - \lambda_0 \int d^3r F^+(\mathbf{r}, \tau; \mathbf{r}, \tau + 0) F(\mathbf{r}, \tau; \mathbf{r}, \tau + 0) \quad (19)$$

This quantity can be represented neglecting small terms of the relative order  $T/\epsilon_F$  like (10) in the form

$$E_{bcs}^0 = - \int d^3r (2\Delta^* + \lambda_0 F^+(\mathbf{r}, \tau; \mathbf{r}, \tau + 0) F(\mathbf{r}, \tau; \mathbf{r}, \tau + 0)) \quad (20)$$

and can be calculated by the expansion in  $\Delta$  of the proper Green functions.

Because the collisions with the change of  $N_s$  are rare one needs the change of the energy  $E_{bcs}^0$  at relatively small variations of  $\delta N_s$  at the collision

$$\delta\epsilon = \frac{\partial E_{bcs}^0}{\partial N_s} \delta N_s \quad (21)$$

The value of  $\delta N_s$  depends on the type of the relaxation process. In the annihilation of two excitations the change of the electron number in Cooper pairs according to (17) is

$\delta N_s = u_p^2 - v_p^2 + u_{|\mathbf{q}-\mathbf{p}|}^2 - v_{|\mathbf{q}-\mathbf{p}|}^2$ . At the scattering of the excitation with the momentum  $\mathbf{p}$  with the phonon emission with the momentum  $\mathbf{q}$  it is  $\delta N_s = u_p^2 - v_p^2 - u_{|\mathbf{p}-\mathbf{q}|}^2 + v_{|\mathbf{p}-\mathbf{q}|}^2$ . The energy balance at the annihilation process is defined by

$(\epsilon_p + \epsilon_{|\mathbf{q}-\mathbf{p}|} - \delta\epsilon(\mathbf{p}, \mathbf{q}) - \omega_q) = 0$  where  $\omega_q$  is the phonon energy.

In the process of phonon scattering the energy balance in the scattering is  $\epsilon_p - \epsilon_{|\mathbf{p}-\mathbf{q}|} - \omega_q - \delta\epsilon(\mathbf{p}, \mathbf{q}) = 0$

The further consideration of the annihilation and the scattering processes does not alter essentially compare to the uniform case [8]. The vertex for the probability of the proper collision can be found in ([12]) with the changed law for the conservation of the energy. The evolution of the  $N_s$  in time will be described by the equation

$$\frac{dN_s}{dt} = \int d^3r W^r(\mathbf{p}, \mathbf{q}) [u^2(p) - v^2(p) + u^2(|\mathbf{q} - \mathbf{p}|) - v^2(|\mathbf{q} - \mathbf{p}|)] \frac{d^3p}{2\pi^3} \frac{d^3p'}{2\pi^3} \\ + 2 \int d^3r W^s(\mathbf{p}, \mathbf{q}) [u^2(p) - v^2(p) - u^2(|\mathbf{p} - \mathbf{q}|) + v^2(|\mathbf{p} - \mathbf{q}|)] \frac{d^3p}{2\pi^3} \frac{d^3p'}{2\pi^3}$$

The values of the scattering probabilities  $W^r$ ,  $W^s$  in the unit of the time and the volume are calculated by the perturbation theory in electron phonon interaction.

Taking into account the change in the energy conservation law they acquire the form

$$W^r(\mathbf{p}, \mathbf{q}) = -\frac{2\pi^3\eta\hbar^2cq}{mp_F} \frac{1}{T} \frac{\partial E_{bcs}^0}{\partial N_s} . \quad (23)$$

$$\cdot [u(|\mathbf{q} - \mathbf{p}|)v(p) + u(p)v(|\mathbf{q} - \mathbf{p}|)]^2 [u^2(p) - v^2(p) + u^2(|\mathbf{q} - \mathbf{p}|) - v^2(|\mathbf{q} - \mathbf{p}|)] [1 - n(p)] [1 - n(|\mathbf{q} - \mathbf{p}|)] N(q) \delta[\epsilon(p) + \epsilon(|\mathbf{q} - \mathbf{p}|) - cq]$$

and a close expression for  $W^r$  Here  $c$  is the sound velocity,  $\eta$  is the material constant in the electron-phonon interaction [5],  $N(q)$  is the phonon distribution function. These formulae are obtained in the linear approximation in  $\partial E_{bcs}^0 / T_c \partial N_s$ .

In metals  $c \ll p_F/m$  that simplifies the calculation of the integrals in the right side of (22). It turns out that in both cases the energy of one excitation is large (of the order of  $T$ ). The other excitation has a small energy of the order of  $|\Delta|$ . That gives the expression for the evolution equation in the form

$$\frac{\partial N_s}{\partial t} = -\frac{mp_F}{4\pi\hbar^3 T_c} \frac{\partial E_{bcs}^0}{\partial N_s} \frac{1}{\tau_{ph}} \int d^3r |\Delta(N_s, r)| \quad (24)$$

This equation is obtained by the assumption that the thermalization of the excitations is rapid compare to the rare relaxation scatterings valid in the Ginsburg-Landau region near  $T_c$ . Therefore we have considered only the quasistationary states for the gap function. The other assumption on the spherical symmetry of the superconducting nuclei can be possibly invalidated at the large enough size of the nuclei because a non spherical form can give the faster growth of  $N_s$ .

The equation (24) simplifies for the uniform relaxation of the order parameter in the whole volume of the superconductor where the quantity  $\frac{\partial E_{BCS}^0}{\partial N_s}$  can be calculated in the terms of the current value of  $|\Delta|$  [8]. In this case (24) can be represented in the form of evolution equation for  $|\Delta|$

$$\frac{\partial(|\Delta| - |\Delta_{eq}|)}{\partial t} = - \frac{|\Delta| - |\Delta_{eq}|}{\tau_r} \quad (25)$$

here

$$\frac{1}{\tau_r} = \frac{|\Delta| + |\Delta_{eq}|}{8T_c} \frac{\pi}{\tau_{ph}}.$$

This equation coincides up to numerical constant with the real part of the so called equation of TDGL obtained in [13] at a different conditions (e.g. the magnetic impurities). Obtained in the presented work the relaxation time is approximately 0,34 of the relaxation time in TDGL equation.

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