Eur. Phys. J. B **61**, 33–45 (2008)
DOI: 10.1140/epjb/e2008-00028-x

THE EUROPEAN PHYSICAL JOURNAL B

The ground state and the thermodynamics of an extended BCS model of superconductivity

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Received 14 March 2007 / Received in final form 13 October 2007
Published online 18 January 2008 –

Abstract. The thermodynamics of an extended BCS model of superconductivity is investigated. A physical system is described by a Hamiltonian containing the BCS interaction and an attractive four-fermion interaction. The four-fermion potential is caused by attractions between Cooper pairs mediated by the phonon field. The weakness of this potential allows the use of perturbation theory. The perturbation expansion was restricted to the first order because in the ground state the second order terms are not larger than 0.5 percent of first order correction for parameters used for calculations. The BCS Hamiltonian is an unperturbed one. The ground state and the thermal properties are examined. As a result the jump in the specific heat is higher than that in the BCS case. Moreover, the squared critical field is larger than the corresponding one in the BCS theory. Additionally, we show connections with the Bogolyubov's mean field approach used earlier in order to investigate general physical consequences of the model.

PACS. 74.20.-z Theories and models of superconducting state – 74.20.Fg BCS theory and its development

1 Introduction

Over the past decades many new phenomena have been discovered (e.g., high temperature superconductivity, heavy fermion superconductors and unusual properties of ^{3}He). These discoveries are still intriguing and lead to new questions on the nature of superconductivity and superfluidity. The problem of the internal symmetry of gap parameters is one such a question. Furthermore, how many particles are involved in constituting the basic clusters responsible for the occurrence of new phases? Are only two-particle interactions relevant to these systems (e.g., Cooper pairs [1,2]) or can three or four-particle structures also be taken into account? The last question was addressed in [3]. In that paper we focused on the derivation of four fermion interactions by making use of a new canonical transformation to the Fröhlich's Hamiltonian completed with the terms proportional to the third power of electron-phonon coupling. After some reducing procedures we obtained the following Hamiltonian

$$H = H_{BCS} + V_4,$$

where

$$H_{BCS} = \sum_{\mathbf{k}\sigma} \xi_{\mathbf{k}} a^*_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma} - |\Lambda|^{-1} \sum_{\mathbf{k},\mathbf{k}'} G_{\mathbf{k}\mathbf{k}'} a^*_{\mathbf{k}+} a^*_{-\mathbf{k}-} a_{-\mathbf{k}'-} a_{\mathbf{k}'+}.$$

The reduced four-fermion interaction V_4 reads

$$V_4 = -|\Lambda|^{-1} \sum_{\mathbf{k},\mathbf{k}'} g_{\mathbf{k}\mathbf{k}'} b^*_{\mathbf{k}} b^*_{-\mathbf{k}} b_{-\mathbf{k}'} b_{\mathbf{k}'}, \qquad (1.1)$$

where

$$b_{\mathbf{k}} = a_{\mathbf{k}+} a_{\mathbf{k}-}$$

and operators $a_{\mathbf{k}\sigma}$, $a^*_{\mathbf{k}\sigma}$ denote the annihilation and creation operators, respectively. $|\Lambda|$ is the volume of the system and $\xi_{\mathbf{k}}$ denotes one-electron energy. This potential describes the interaction between the Cooper pairs with momenta and spins $\{\mathbf{k}+, -\mathbf{k}-\}$ and $\{-\mathbf{k}+, \mathbf{k}-\}$.

Moreover, we were able to find the sign and the approximated form of coupling constant of the four-fermion interaction

$$g_{\mathbf{k}_F\mathbf{k}_F} \approx \frac{D^6_{\mathbf{k}_F}}{\hbar^5 \omega^5_{\mathbf{k}_F}},$$

where $D_{\mathbf{k}_F}$ and $\hbar\omega_{\mathbf{k}_F}$ are the electron-phonon coupling constant and the phonon energy at Fermi level, respectively. The relationship between this coupling constant and BCS coupling constant was estimated to be

$$g_{\mathbf{k}_F\mathbf{k}_F} = \frac{G^3_{\mathbf{k}_F\mathbf{k}_F}}{\hbar^2 \omega^2_{\mathbf{k}_F}}.$$

This relationship points to the weak character of the quadruple interaction in comparison to familiar Cooper

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pairing. In classical superconductors such an effect cannot be observed due to weak BCS coupling and too strong Coulomb repulsion between electrons. However, in materials with strong coupling between electrons and phonons such an effect could be visible and recognizable especially from surveys of magnetic flux quanta. It is widely accepted that if half-$h/2e$ magnetic flux quanta appear among usual ones it points to the existence of quadruples in an investigated system. In this paper we strive to answer the question what the influence of quadruples on the BCS system and its thermodynamics is. Is it possible to grasp some distinctive features which can help in recognition the presence of quadruples in a physical system?

This issue has become more and more interesting due to some discoveries and suggestions. Namely, in 1993 Schneider and Keller [4] measured the relationship between the critical temperature and zero temperature condensate density of some cuprates and Chevrel-phases superconductors. They noticed that the experimental data for $Y\mathrm{Ba_2Cu_3O_{6.602}}$, for example, point to the behavior of a dilute Bose gas. As a result they suggested Bose condensation of weakly interacting fermion pairs as a mechanism of transition from the normal to the superconducting state. Moreover, a discovery of Bunkov et al. [5] points to the presence of fermion quadruples in ^{3}He. Their work was devoted to the problem of the influence of spatial disorder on the order parameter in superfluid ^{3}He. The authors, quoting Volovik [6], suggested that unusual spectra of ^{3}He in aerogel could be explained by a process in which impurities tend to destroy the anisotropic correlations of the order parameter, while correlations of higher symmetry can survive (e.g. four-particle correlations). Two papers [7,8] report a discovery of the half-$h/2e$ magnetic flux quanta coexisting together with the usual ones in SQUIDs fabricated of bicrystalline $Y\mathrm{Ba_2Cu_3O_{7-\delta}}$ films. As is known, this situation corresponds to the presence of fermion quadruples in a physical system and points to taking the interplay between Cooper pairs and quadruples into consideration. It is worthwhile to mention that there were some attempts of introducing the four-fermion interactions to the nuclear physics [9].

The BCS theory [1] is still very significant to this problem and can serve as a frame of our considerations. In this frame [10] we investigated earlier the system with Cooper's pairs and quadruples making use of the Bogolyubov's mean field approach. In that paper it was assumed that

$$G_{\mathbf{k}\mathbf{k}'} = G\chi(\mathbf{k})\chi(\mathbf{k}'),\ \ G>0,\ \ g_{\mathbf{k}\mathbf{k}'} = g\chi(\mathbf{k})\chi(\mathbf{k}'),\ \ g>0,$$

with $\chi(\mathbf{k})$ denoting the characteristic function of the set $\{\mathbf{k} : -\delta < \xi_k < \delta\}$ for $\xi_k = \frac{\hbar^2 k^2}{2m} - \mu$ and fixed δ. Moreover, μ denotes the chemical potential. A structure of excited states and the ground state were examined. Moreover, a preliminary insight into thermodynamics of this system was done but the resulting expressions for two order parameters and the statistical sum were too complicated to be analyzed in detail. For instance, the equations for the BCS and quadruple order parameters, which were assumed to be real, proved to be coupled and impossible to be solved in the general case. It should be added that these expressions are exact in the thermodynamic limit [11], however, the mathematical complexity of the problem made the thermodynamics of this Hamiltonian almost entirely obscure. Therefore there appeared a need for looking for an approximated method to investigate the thermodynamics. It turned out that it could be done by making use of perturbation theory. The BCS system can be an unperturbed one and V_4 a perturbation. In this paper the ground state and equilibrium properties were investigated for the intermediate coupling. Additionally, the analytical forms of some thermodynamic functions in the vicinity of T_c and $T=0$ were found for the weak coupling regime. It was shown that the jump in the specific heat is higher than that of the BCS case. Moreover, the squared critical magnetic field exceeds that for the BCS case. Next, we confront the results obtained for the ground state with those obtained in the frame of the Bogolyubov's mean field method [14,15]. This method is more general than perturbation theory used in the paper in the sense that the Bogolyubov's approach comprises directly the influence of quadruples on the Cooper pairs due to the coupling all the order parameters. Furthermore, it can be used even to cases in which the quadruple interaction is not so weak in comparison to the BCS one. However, when the quadruple gap is much smaller than the BCS one the effect of their coupling is negligible and the agreement between two approaches is obtained.

2 The ground state

We aim at obtaining the first order corrections to the ground state BCS energy. The system is described by the following Hamiltonian

$$H = H_0 + V_4,$$

where $H_0 = H_{BCS}$. The potential V_4 is assumed to be much smaller than the BCS interaction and is treated as a perturbation. The BCS ground state vector is used in the following form

$$|BCS\rangle = \prod_{\mathbf{k}>0} |\mathbf{k}BCS\rangle = \prod_{\mathbf{k}>0} (u_{\mathbf{k}}^2 + u_{\mathbf{k}} v_{\mathbf{k}} (a^*_{\mathbf{k}+} a^*_{-\mathbf{k}-} - a^*_{\mathbf{k}-} a^*_{-\mathbf{k}+}) - v_{\mathbf{k}}^2 a^*_{\mathbf{k}+} a^*_{\mathbf{k}-} a^*_{-\mathbf{k}+} a^*_{-\mathbf{k}-}) |0\rangle, \quad (2.1)$$

where the product is over a fixed half-space of $\boldsymbol{R}^3$. $|u_{\mathbf{k}}|^2 = \frac{1}{2}(1+\frac{\xi_k}{E_{\mathbf{k}}})$, $|v_{\mathbf{k}}|^2 = \frac{1}{2}(1-\frac{\xi_k}{E_{\mathbf{k}}})$ are the well-known variational parameters [2], where $E_{G\mathbf{k}} = \sqrt{\xi_{\mathbf{k}}^2 + |\Delta_{\mathbf{k}G}|^2}$, with complex $\Delta_{\mathbf{k}G} := |\Lambda|^{-1} \sum_{\mathbf{k}'} G_{\mathbf{k}\mathbf{k}'} u^*_{\mathbf{k}'} v_{\mathbf{k}'}$ and single-electron energies $\xi_{\mathbf{k}}$ are measured from the chemical potential μ. In order to obtain the first order correction we need to calculate the expectation value of V_4 in the BCS ground state, namely

$$E_g = \langle BCS|V_4|BCS\rangle = -|\Lambda|^{-1} \sum_{\mathbf{k},\mathbf{k}'} g_{\mathbf{k}\mathbf{k}'} (u^*_{\mathbf{k}} v_{\mathbf{k}})^2 (u_{\mathbf{k}'} v^*_{\mathbf{k}'})^2. \quad (2.2)$$

Let us define now a new parameter in the following form

$$\Delta^*_{\mathbf{k}g} := -|\Lambda|^{-1}\sum_{\mathbf{k}'} g_{\mathbf{k}\mathbf{k}'}(u_{\mathbf{k}'}v^*_{\mathbf{k}'})^2 = -|\Lambda|^{-1}\sum_{\mathbf{k}'} g_{\mathbf{k}\mathbf{k}'}\frac{\Delta^*_{\mathbf{k}'G}\Delta^*_{\mathbf{k}'G}}{4(\xi^2_{\mathbf{k}'}+|\Delta_{\mathbf{k}'G}|^2)}. \quad (2.3)$$

The new parameter can be regarded as an complex order parameter corresponding to quadruples. Quadruples appear as a result of the interactions between Cooper pairs [3]. The four-fermion interaction is mediated by the phonon field and is significantly weaker than the BCS interaction. The appearance of quadruples is entirely determined by the existence of Cooper pairs in the system. Without Cooper pairs quadruples cannot exist in this case. Having defined the new parameter we can now express the correction term in terms of this parameter and write down the total energy of the system, namely

$$E_0 = E_{BCS} + \frac{1}{4}\sum_{\mathbf{k}}\frac{\Delta_{\mathbf{k}g}\Delta^*_{\mathbf{k}G}\Delta^*_{\mathbf{k}G}}{\xi^2_{\mathbf{k}}+|\Delta_{\mathbf{k}G}|^2} = E_{BCS} - |\Lambda|\frac{|\Delta_g|^2}{g}. \quad (2.4)$$

It is evident from the equation above that $E_0 < E_{BCS}$.

The question arises what the properties of the new gap parameter are? To answer this question let us replace the sum with an integral in the equation (2.3). Finally, we obtain

$$\Delta_g = -g\rho_F\frac{1}{4}\Delta^2_G\int_{-\delta}^{\delta}\frac{d\xi}{(\xi^2+|\Delta_G|^2)} = -g\rho_F\frac{1}{2}\frac{\Delta^2_G}{|\Delta_G|}\arctan\frac{\delta}{|\Delta_G|}. \quad (2.5)$$

We exploited here the assumptions regarding the range of both interactions presented in the Introduction as well as the independence of the order parameters of the momentum vector. Moreover, the standard approximation for the density of states $\rho(\xi) \approx \rho_F$, where ρ_F is the density of states for a free electron gas at the Fermi level, was used. Now let us look at two opposite limits of $|\Delta_g|$, namely, $|\Delta_G| \to \infty$ and $|\Delta_G| \to 0$. In the former case it is obvious that in this limit the absolute value $|\Delta_g| = \frac{g\rho_F\delta}{2}$. In the latter case $|\Delta_g| = 0$ is obtained. The second result is not surprising; however, the first limit means that there is a saturation of the gap for quadruples and despite the increase of the strength of BCS pairing mechanisms the gap of quadruples does not increase further. It is worthwhile to note that Δ_g is a linear function of $g\rho_F$. This means that in the case of very weak interactions between fermion pairs the contribution of these interactions to the ground state energy is weaker, correspondingly.

The next problem is what happens to the chemical potential when quadruples coexist with Cooper pairs in the system. The ground state energy takes the following form

$$E_0 = \sum_{\mathbf{k}>0}\left[2\xi_{\mathbf{k}} - E_{\mathbf{k}} - \frac{\xi^2_{\mathbf{k}}}{E_{\mathbf{k}}} + \frac{1}{2}\frac{\Delta_{\mathbf{k}g}\Delta^*_{\mathbf{k}G}\Delta^*_{\mathbf{k}G}}{\xi^2_{\mathbf{k}}+|\Delta_{\mathbf{k}G}|^2}\right]$$

or

$$E_0 = \sum_{\mathbf{k}>0}\left[2\xi_{\mathbf{k}} - 2E_{\mathbf{k}} + \frac{|\Delta_{\mathbf{k}G}|^2}{E_{\mathbf{k}}} + \frac{1}{4}\frac{\Delta_{\mathbf{k}g}\Delta^*_{\mathbf{k}G}\Delta^*_{\mathbf{k}G} + \Delta^*_{\mathbf{k}g}\Delta_{\mathbf{k}G}\Delta_{\mathbf{k}G}}{\xi^2_{\mathbf{k}}+|\Delta_{\mathbf{k}G}|^2}\right]. \quad (2.6)$$

It is known that the average number of electrons in the ground state can be obtained from

$$N = -\frac{\partial E_0}{\partial\mu}.$$

Differentiation of the ground state energy yields

$$N = \sum_{\mathbf{k}}\left[1 - \frac{1}{2}\frac{\xi_{\mathbf{k}}}{E_{\mathbf{k}}} - \frac{2\xi_{\mathbf{k}}E^2_{\mathbf{k}} - \xi^3_{\mathbf{k}}}{2E^3_{\mathbf{k}}} + \frac{\xi_{\mathbf{k}}(\Delta_{\mathbf{k}g}\Delta^*_{\mathbf{k}G}\Delta^*_{\mathbf{k}G} + \Delta^*_{\mathbf{k}g}\Delta_{\mathbf{k}G}\Delta_{\mathbf{k}G})}{4(\xi^2_{\mathbf{k}}+|\Delta_{\mathbf{k}G}|^2)^2}\right], \quad (2.7)$$

where summation is over the whole momentum space. After a few simple steps, where we used the fact that some functions in the expression above are odd functions of ξ, it yields

$$N = \sum_{\mathbf{k}:\xi_{\mathbf{k}}<-\delta} 2 + 2|\Lambda|\rho_F\delta,$$

that implies $\mu = E_F$ as it is in the BCS theory [12]. E_F denotes the Fermi energy of a free electron gas.

An important remark should be made here. We restricted the perturbation expansion to the first order term. The second order terms give the contributions of order 0.5 percent of the first order one. Moreover, the form of the quadruple gap and the correction to the ground state energy does not contain a difficulty inherent in the BCS theory. As is remembered this difficulty leads to the divergence in the perturbation series with respect to the BCS coupling constant and makes such a perturbation expansion unfeasible in the BCS theory.

3 The excited states

Now we would like to look at the excitation spectrum for the BCS case written in terms of the ground state vector (2.1). We follow the standard route [12] introducing the Bogolyubov-Valatin transformation with complex coefficients

$$\begin{aligned}\alpha^*_{\mathbf{k}1} &= u_{\mathbf{k}}a^*_{\mathbf{k}1} - v_{\mathbf{k}}a_{\mathbf{k}4}\,, & \alpha^*_{\mathbf{k}2} &= u_{\mathbf{k}}a^*_{\mathbf{k}2} + v_{\mathbf{k}}a_{\mathbf{k}3}\\ \alpha^*_{\mathbf{k}3} &= u_{\mathbf{k}}a^*_{\mathbf{k}3} - v_{\mathbf{k}}a_{\mathbf{k}2}\,, & \alpha^*_{\mathbf{k}4} &= u_{\mathbf{k}}a^*_{\mathbf{k}4} + v_{\mathbf{k}}a_{\mathbf{k}1},\end{aligned}$$

where a new notation concerning indices was used: $\mathbf{k}1 = \mathbf{k}+$, $\mathbf{k}2 = \mathbf{k}-$, $\mathbf{k}3 = -\mathbf{k}+$, $\mathbf{k}4 = -\mathbf{k}-$. Of course, the operators α satisfy the following equation

$$\alpha|BCS\rangle = 0.$$

$$\rho_{BCS} := \prod_{\mathbf{k}>0} \frac{P_{\mathbf{k}BCS} + e^{-\beta E_{G\mathbf{k}}} \sum_{i=1}^{4} P_{\mathbf{k}i} + e^{-2\beta E_{G\mathbf{k}}} \sum_{i<j} P_{\mathbf{k}ij} + e^{-3\beta E_{G\mathbf{k}}} \sum_{i<j<l} P_{\mathbf{k}ijl} + e^{-4\beta E_{G\mathbf{k}}} P_{\mathbf{k}1234}}{(1+e^{-\beta E_{G\mathbf{k}}})^4},$$

The normalized $\mathbf{k}$-excited states are shown in Appendix A. Making use of them it is easy to check that the excitation energies are as follows

$$\langle \mathbf{k}i|H|\mathbf{k}i\rangle - E_{\mathbf{k}BCS} = E_{G\mathbf{k}}, \tag{3.1}$$

$$\langle \mathbf{k}ij|H|\mathbf{k}ij\rangle - E_{\mathbf{k}BCS} = 2E_{G\mathbf{k}}, \tag{3.2}$$

$$\langle \mathbf{k}ijl|H|\mathbf{k}ijl\rangle - E_{\mathbf{k}BCS} = 3E_{G\mathbf{k}}, \tag{3.3}$$

$$\langle \mathbf{k}1234|H|\mathbf{k}1234\rangle - E_{\mathbf{k}BCS} = 4E_{G\mathbf{k}}, \tag{3.4}$$

where $i,j,l \in \{1,2,3,4\}$. This result was expected to be obtained and now one can proceed towards the thermodynamics. As is known, this excitation spectrum serves for constructing the density matrix for the BCS system.

4 The thermodynamics

Now we can follow the standard procedure [2,12] and construct the density matrix for the unperturbed system

See equation above.

where the operators P are projectors defined as follows

$$\begin{aligned} P_{\mathbf{k}BCS} &:= |\mathbf{k}BCS\rangle\langle BCS\mathbf{k}|,\\ P_{\mathbf{k}i} &:= |\mathbf{k}i\rangle\langle i\mathbf{k}|,\\ P_{\mathbf{k}ij} &:= |\mathbf{k}ij\rangle\langle ij\mathbf{k}|,\\ P_{\mathbf{k}ijl} &:= |\mathbf{k}ijl\rangle\langle ijl\mathbf{k}|,\\ P_{\mathbf{k}1234} &:= |\mathbf{k}1234\rangle\langle 1234\mathbf{k}|. \end{aligned}$$

Of course, this density matrix is entirely equivalent to that one used in [2,12]. To make the calculations more convenient let us introduce new functions:

$$f_{\mathbf{k}1} := \frac{4e^{-\beta E_{G\mathbf{k}}}}{M_{\mathbf{k}}}, \qquad f_{\mathbf{k}2} := \frac{6e^{-2\beta E_{G\mathbf{k}}}}{M_{\mathbf{k}}},$$

$$f_{\mathbf{k}3} := \frac{4e^{-3\beta E_{G\mathbf{k}}}}{M_{\mathbf{k}}}, \qquad f_{\mathbf{k}4} := \frac{e^{-4\beta E_{G\mathbf{k}}}}{M_{\mathbf{k}}},$$

where $M_{\mathbf{k}} := (1+e^{-\beta E_{G\mathbf{k}}})^4 = 1 + 4e^{-\beta E_{G\mathbf{k}}} + 6e^{-2\beta E_{G\mathbf{k}}} + 4e^{-3\beta E_{G\mathbf{k}}} + e^{-4\beta E_{G\mathbf{k}}}$. The density matrix of the BCS system in terms of these functions is

$$\rho_{BCS} := \prod_{\mathbf{k}>0}\left[\left(1-\sum_{i=1}^{4} f_{\mathbf{k}i}\right)P_{\mathbf{k}BCS} + \frac{1}{4} f_{\mathbf{k}1}\sum_{i=1}^{4} P_{\mathbf{k}i} + \frac{1}{6} f_{\mathbf{k}2}\sum_{i<j} P_{\mathbf{k}ij} + \frac{1}{4} f_{\mathbf{k}3}\sum_{i<j<l} P_{\mathbf{k}ijl} + f_{\mathbf{k}4} P_{\mathbf{k}1234}\right]. \tag{4.1}$$

Having the density matrix at our disposal we can address the problem of the thermodynamic functions of the total system. As is known, (e.g., [13]) it is possible to expand the free energy in the perturbation series, namely

$$\mathcal{F}_s = \mathcal{F}_{BCS} + \operatorname{Tr}\rho_{BCS} V_4 + \ldots \tag{4.2}$$

We are only interested in the first order corrections due to the arguments concerning the second order corrections in the ground state used in Section 3. It is supposed here that the latter are not important at finite temperatures as it is at $T=0$. Therefore, it suffices to calculate the expectation value of the operator V_4 in the state ρ_{BCS}. One obtains

$$\operatorname{Tr}\rho_{BCS}V_4 = -|\Lambda|^{-1}\sum_{\mathbf{k},\mathbf{k}'} g_{\mathbf{k}\mathbf{k}'}(u^*_{\mathbf{k}}v_{\mathbf{k}})^2(u_{\mathbf{k}'}v^*_{\mathbf{k}'})^2 \times\left(1-f_{\mathbf{k}1}-\frac{4}{3}f_{\mathbf{k}2}-f_{\mathbf{k}3}\right)\left(1-f_{\mathbf{k}'1}-\frac{4}{3}f_{\mathbf{k}'2}-f_{\mathbf{k}'3}\right), \tag{4.3}$$

which leads to

$$\operatorname{Tr}\rho_{BCS}V_4 = \sum_{\mathbf{k}} \Delta_{\mathbf{k}g}\frac{\Delta^*_{\mathbf{k}G}\Delta^*_{\mathbf{k}G}}{4E^2_{\mathbf{k}}}\left(1-f_{\mathbf{k}1}-\frac{4}{3}f_{\mathbf{k}2}-f_{\mathbf{k}3}\right), \tag{4.4}$$

where the gap parameter for quadruples was introduced, namely

$$\Delta_{\mathbf{k}g} := -|\Lambda|^{-1}\sum_{\mathbf{k}'} g_{\mathbf{k}\mathbf{k}'}(u^*_{\mathbf{k}'}v_{\mathbf{k}'})^2\left(1-f_{\mathbf{k}'1}-\frac{4}{3}f_{\mathbf{k}'2}-f_{\mathbf{k}'3}\right).$$

The expression above can be transformed to the following form

$$\Delta_{\mathbf{k}g} = -|\Lambda|^{-1}\sum_{\mathbf{k}'} g_{\mathbf{k}\mathbf{k}'}\frac{\Delta_{\mathbf{k}'G}\Delta_{\mathbf{k}'G}}{4E^2_{\mathbf{k}'}}\left(\tanh\frac{1}{2}\beta E_{\mathbf{k}'}\right)^2. \tag{4.5}$$

As is seen, the quadruple gap equation is modified by the presence of $\left(\frac{\tanh\frac{1}{2}\beta E_{\mathbf{k}}}{E_{\mathbf{k}}}\right)^2$ in the integral which is the product of two BCS contributions. Moreover, it is possible to deduce at this stage of the considerations that both the Cooper pairs and the quadruples have the same critical temperature. If only the BCS gap vanishes the quadruple gap does as well.

At this stage the free energy reads

$$\mathcal{F}_s = \mathcal{F}_{BCS} + \frac{1}{2}\sum_{\mathbf{k}}\frac{\Delta^*_{\mathbf{k}g}\Delta_{\mathbf{k}G}\Delta_{\mathbf{k}G} + \Delta_{\mathbf{k}g}\Delta^*_{\mathbf{k}G}\Delta^*_{\mathbf{k}G}}{4E^2_{\mathbf{k}}}\left(\tanh\frac{1}{2}\beta E_{\mathbf{k}}\right)^2 \tag{4.6}$$

We can now proceed towards the addressing the next problem. It is known from general thermodynamics that there exists a relationship between the free energy and the critical magnetic field H_c. It reads

$$|\Lambda|\frac{H_c^2}{8\pi} = \mathcal{F}_n - \mathcal{F}_s, \tag{4.7}$$

where $\mathcal{F}_n$ is the free energy in the normal state. It is easy to show that after passing to the thermodynamic limit we have in the ground state

$$\frac{H_c^2}{8\pi} = -\rho_F\delta^2 + \rho_F\delta\sqrt{\delta^2+|\Delta_G|^2} + \rho_F\frac{|\Delta_g|^2}{g\rho_F},$$

where the first two terms are BCS and the last one is the quadruple correction. This points to the larger critical magnetic field than in the BCS theory. This fact can be explained by the necessity of introducing some additional amount of energy in order to destroy quadruples and Cooper pairs because more energy is involved in bindings between fermions at this stage.

5 Numerical results

Obviously we are not able to calculate all thermodynamic functions analytically for finite temperatures and we are forced to use numerical methods. At first, we need to solve two equations for both gaps, namely

$$\frac{2}{G\rho_F} = \int_{-\delta}^{\delta}\frac{d\xi}{E_G}\tanh\left(\frac{1}{2}\beta_c t^{-1}E_G\right), \tag{5.1}$$

$$|\Delta_g| = \frac{1}{4}g\rho_F|\Delta_G|^2\int_{-\delta}^{\delta}\frac{d\xi}{E_G^2}\left(\tanh(\frac{1}{2}\beta_c t^{-1}E_G)\right)^2, \tag{5.2}$$

where $\beta_c = 1/k_BT_c$, $E_G = \sqrt{\xi^2+|\Delta_G|^2}$ and $t = \frac{T}{T_c}$ is a reduced temperature. Fortunately, they can be solved separately. To find the critical temperature it suffices to solve (5.1) for $t = 1$ and $\Delta_G = 0$. The numerical calculations were done for the following set of parameters: The Fermi energy $E_F = 0.5$ eV, $\delta = 0.01$ eV, $G\rho_F = 1$, $g\rho_F = 0.05$. $T_c = 51.73$ K ($\beta_c = 224.382$ eV^{-1}) was obtained. The ground state values of the gap parameters are: $|\Delta_G(0)| = \frac{\delta}{\sinh\frac{1}{G\rho_F}} = 0.008509$ eV and $|\Delta_g(0)| = 0.00018417$ eV. It is seen that the BCS gap is about two orders of magnitude greater than the quadruple one. The graphs of both gap parameters divided by their corresponding ground state values versus the reduced temperature are presented in Figure 1. The quadruple gap curve starts to decrease earlier than the BCS one when the temperature is increased to the critical temperature. Moreover, the quadruple gap is a linear function of the temperature in the vicinity of T_c.

Now it is worthwhile to undertake the problem of the validity of the choice $\frac{g}{G} = 0.05$. If we agree that $\hbar\omega_{k_F} \approx \delta$ then $\delta \approx v_s\sqrt{2mE_F}$, where v_s denotes the velocity of sound and m the electron mass. This leads to $v_s \approx 4.4\times 10^3\frac{m}{s}$ what means a sufficiently good agreement with values of that velocity in the solid state physics

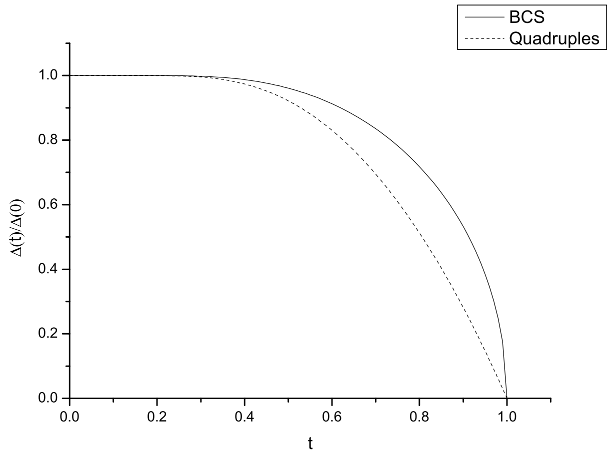

Fig. 1. The ratio $\frac{\Delta(t)}{\Delta(0)}$ plotted for the pure BCS system and the system with the Cooper pairs and quadruples. The continuous curve corresponds to the BCS gap parameter divided by its value at $t = 0$. The dashed curve corresponds to the quadruple gap parameter divided by its value at $t = 0$. The former is plotted according to equation (5.1) and the latter according to equations (5.1) and (5.2). The appearance of the BCS gap at T_c entails the appearance of the quadruple gap. The quadruple gap is a linear function of the temperature in the vicinity of T_c.

at least to the order of magnitude. Moreover, if one notices that $\frac{g}{G} = \left(\frac{D_{k_F}}{\delta}\right)^4$ then $\frac{D_{k_F}}{\delta} = \left(\frac{g}{G}\right)^{\frac{1}{4}}$ that leads to the obvious inequality $D_{k_F} < \delta \ll E_F$. Both of the results point to the dominating role of the Fermi energy in the system; therefore the Migdal's theorem is not violated and the normal Fermi liquid description of the normal phase is correct.

The free energy density is calculated by using the following expression

$$\frac{f(t)}{c_n(T_c)T_c} = \frac{f_{BCS}(t)}{c_n(T_c)T_c} - \frac{3}{2\pi^2}\frac{\beta_c^2}{g\rho_F}|\Delta_g|^2 \tag{5.3}$$

with the BCS free energy density

$$\begin{aligned}\frac{f_{BCS}(t)}{c_n(T_c)T_c} &= \\ &-\frac{3}{\pi^2}E_F^{-\frac{1}{2}}\beta_c^2\Bigg[t\beta_c^{-1}\int_{-E_F}^{-\delta}d\xi\sqrt{\xi+E_F}\ln(1+e^{\beta_c t^{-1}\xi}) \\ &+t\beta_c^{-1}\int_{\delta}^{\infty}d\xi\sqrt{\xi+E_F}\ln(1+e^{-\beta_c t^{-1}\xi}) + t\beta_c^{-1}\sqrt{E_F} \\ &\times\int_{-\delta}^{\delta}d\xi\ln(1+e^{-\beta_c t^{-1}E_G}) + \frac{1}{2}\sqrt{E_F}\delta\sqrt{\delta^2+|\Delta_G^2|} \\ &+\frac{1}{2}|\Delta_G|^2\int_{-\delta}^{\delta}\frac{d\xi}{E_G}\frac{1}{1+e^{\beta_c t^{-1}E_G}}\Bigg] + C,\end{aligned} \tag{5.4}$$

where C is a constant, $c_n(T_c) = \frac{2}{3}\pi^2\rho_F T_c k_B^2$ denotes the specific heat for the free electron gas at T_c. The graphs of the free energy density for the pure BCS system, the mixed system (when both interactions are present) and normal one are plotted in Figure 2. The shape of the curve for the mixed state is very similar to that of the BCS system and is slightly below the latter. This means that the free energy of the system with two interactions is lower than the BCS free energy.

Now we proceed to the entropy density. This thermodynamic function can be calculated from

$$\frac{s(t)}{c_n(T_c)} = \frac{s_{BCS}(t)}{c_n(T_c)} + \frac{3}{\pi^2}\frac{\beta_c^2}{g\rho_F}|\Delta_g|\frac{d|\Delta_g|}{dt}. \tag{5.5}$$

The correction to the entropy density for the BCS system s_{BCS} is negative which follows from $\frac{d|\Delta_g|}{dt} < 0$. The BCS entropy density is

$$\begin{aligned}
&\frac{s_{BCS}}{c_n(T_c)} = \\
&\frac{3}{\pi^2}\beta_c E_F^{-\frac{1}{2}}\left[\int_{-E_F}^{-\delta} d\xi\sqrt{\xi+E_F}\frac{e^{-\beta_c t^{-1}\xi}}{1+e^{-\beta_c t^{-1}\xi}}\ln(1+e^{\beta_c t^{-1}\xi})\right. \\
&+\int_{\delta}^{\infty} d\xi\sqrt{\xi+E_F}\frac{e^{\beta_c t^{-1}\xi}}{1+e^{\beta_c t^{-1}\xi}}\ln(1+e^{-\beta_c t^{-1}\xi}) \\
&+\int_{-E_F}^{-\delta} d\xi\sqrt{\xi+E_F}\frac{1}{1+e^{-\beta_c t^{-1}\xi}}\ln(1+e^{-\beta_c t^{-1}\xi}) \\
&+\int_{\delta}^{\infty} d\xi\sqrt{\xi+E_F}\frac{1}{1+e^{\beta_c t^{-1}\xi}}\ln(1+e^{\beta_c t^{-1}\xi}) \\
&+\frac{1}{2}\sqrt{E_F}\delta\sqrt{\delta^2+|\Delta_G|^2}+\sqrt{E_F}\int_{-\delta}^{\delta} d\xi\frac{e^{\beta_c t^{-1}E_G}}{1+e^{\beta_c t^{-1}E_G}} \\
&\left.\times\ln(1+e^{-\beta_c t^{-1}E_G})+\sqrt{E_F}\int_{-\delta}^{\delta} d\xi\frac{\ln(1+e^{\beta_c t^{-1}E_G})}{1+e^{\beta_c t^{-1}E_G}}\right].
\end{aligned} \tag{5.6}$$

The form of the correction term was derived in Appendix B. The graphs of the entropy density for the mixed, BCS and normal states are plotted in Figure 3. The mixed state is more ordered than the BCS one. That is why the entropy for the state with the Cooper pairs and quadruples is lower than for the pure BCS system. As is seen this entropy is continuous and the system with both interactions present undergoes the second order phase transition.

The next function is the specific heat. It can be obtained from

$$\frac{c(t)}{c_n(T_c)} = \frac{c_{BCS}(t)}{c_n(T_c)} + \frac{3}{2\pi^2}\frac{\beta_c^2}{g\rho_F}t\frac{d^2|\Delta_g|^2}{dt^2}, \tag{5.7}$$

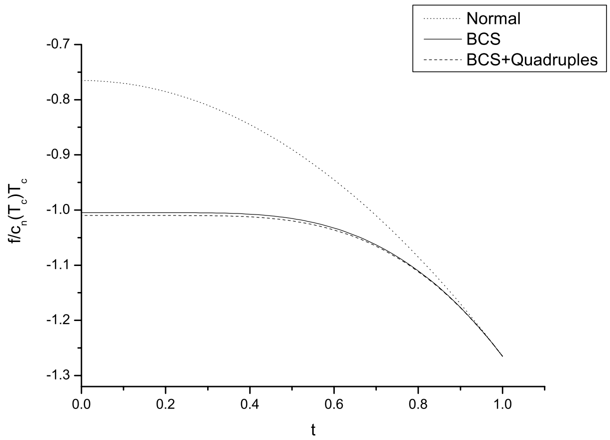

Fig. 2. The free energy density ratios $\frac{f}{c_n(T_c)T_c}$ plotted for the normal, BCS and mixed states. The continuous line corresponds to the pure BCS case. The dashed line corresponds to the mixed system and the dotted to the normal one. The BCS free energy density is plotted according to equation (5.4) whereas the mixed case to equations (5.3) and (5.4).

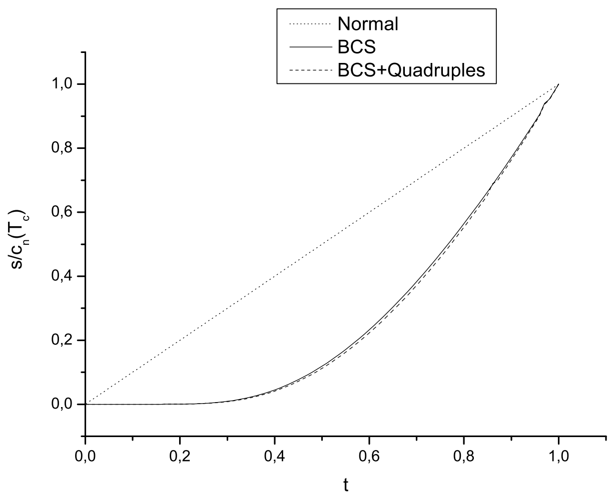

Fig. 3. The entropy density ratios $\frac{s}{c_n(T_c)}$ are plotted for the normal, pure BCS and mixed states. The continuous curve corresponds to the pure BCS case. The dashed line corresponds to the mixed case and the dotted one to the normal case. They were calculated according to equations (5.5) and (5.6).

where

$$\begin{aligned}
&\frac{c_{BCS}(t)}{c_n(T_c)} = \frac{3\beta_c^3}{4\pi^2\sqrt{E_F}t^2}\left[\int_{-E_F}^{-\delta} d\xi\sqrt{\xi+E_F}\frac{\xi^2}{\cosh^2\frac{1}{2}\beta_c t^{-1}\xi}\right. \\
&+\int_{\delta}^{\infty} d\xi\sqrt{\xi+E_F}\frac{\xi^2}{\cosh^2\frac{1}{2}\beta_c t^{-1}\xi}+\sqrt{E_F}\int_{-\delta}^{\delta} d\xi\frac{E_G^2}{\cosh^2\frac{1}{2}\beta_c t^{-1}E_G} \\
&\left.-t|\Delta_G|\frac{d|\Delta_G|}{dt}\sqrt{E_F}\int_{-\delta}^{\delta} d\xi\frac{1}{\cosh^2\frac{1}{2}\beta_c t^{-1}E_G}\right].
\end{aligned} \tag{5.8}$$

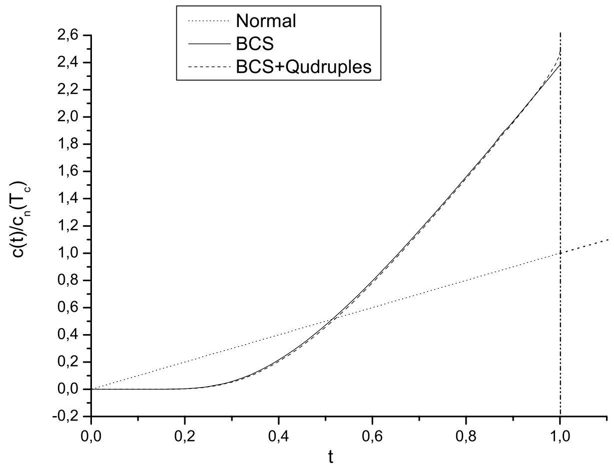

Fig. 4. The specific heat ratios $\frac{c}{c_n(T_c)}$ are plotted for the normal, pure BCS and mixed states. The continuous curve corresponds to the pure BCS case. The dashed line corresponds to the mixed case and the dotted one to the normal case. They were obtained by using (5.7) and (5.8). As is seen there are jumps in the specific heat for the BCS and mixed states. The jump in the BCS case is lower than that in the mixed state case and the difference between them is 0.0975.

The form of the correction to the BCS specific heat c_{BCS} was derived in Appendix B as well and turns out to be positive what implies that the jump for the total system is higher than that in the BCS case. The reader can find the form of $|\Delta_G|\frac{d|\Delta_G|}{dt}$ in that Appendix. The graphs of the specific heat for three cases mentioned above are plotted in Figure 4. In fact, we obtained

$$\left.\frac{c_{BCS}-c_n}{c_n}\right|_{T=T_c} = 1.3826, \tag{5.9}$$

$$\left.\frac{c-c_n}{c_n}\right|_{T=T_c} = 1.4801. \tag{5.10}$$

The difference between them , it is the correction to the BCS specific heat, is equal

$$\left.\frac{\Delta c}{c_n(T_c)}\right|_{T=T_c} = \frac{3}{\pi^2}\beta_c^2 c_0^2 g\rho_F\left[\left.\left(|\Delta_G|\frac{d|\Delta_G|}{dt}\right)\right|_{T=T_c}\right]^2 = 0.0975, \tag{5.11}$$

where

$$c_0 := \lim_{\substack{t\to 1\\ |\Delta_G|\to 0}} \int_0^\delta \frac{d\xi}{E_G^2}\left(\tanh\left((\frac{1}{2}\beta_c t^{-1}E_G\right)\right)^2$$

and

$$\left.\left(|\Delta_G|\frac{d|\Delta_G|}{dt}\right)\right|_{T=T_c} = -\frac{4\delta^2\tanh\frac{1}{2}\beta_c\delta}{\beta_c\delta+\beta_c\delta^2 c_0 - 2\tanh\frac{1}{2}\beta_c\delta}. \tag{5.12}$$

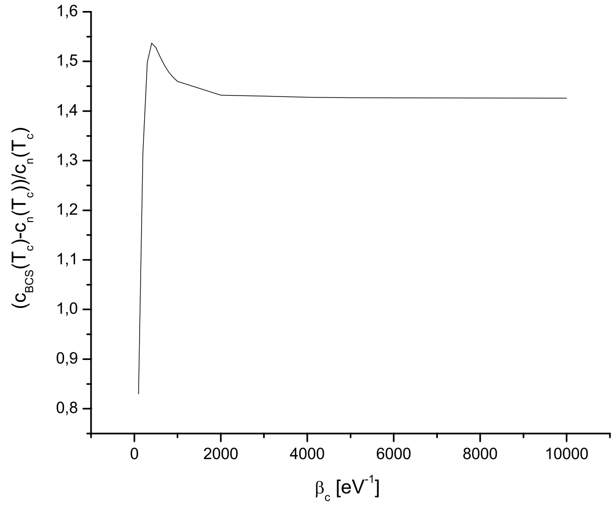

Fig. 5. The height of the BCS specific heat jump versus the inverse of the critical temperature β_c.

The derivation of equations (5.11) and (5.12) is outlined in Appendix B. It is very important to note that the correction to the BCS specific heat and as a consequence the jump are linear in $g\rho_F$ and vanish when $g\rho_F \to 0$. This fact expresses non-universality of the correction. Moreover, it is worthwhile to mention that there is some deviation from the universal values $|\Delta_G(0)|\beta_c = 1.7638...$ and the jump in the BCS theory $\frac{\Delta c}{c_n(T_c)} = 1.426...$ [12]. Here, we obtain $|\Delta_G(0)|\beta_c = 1.9093$ and the BCS jump equal 1.3826 (see Eq. (5.9)). The reason of the deviation is that the calculations concern the intermediate BCS coupling and in this regime the approximations used for the weak-coupling case (e.g., [20]) are not valid. It is easy to check that the jump of the BCS specific heat at T_c is

$$\left.\frac{c_{BCS}-c_n}{c_n}\right|_{T=T_c} = \frac{12\beta_c^2}{\pi^2}\frac{\delta^2\tanh^2\frac{1}{2}\beta_c\delta}{\beta_c\delta+\beta_c\delta^2 c_0 - 2\tanh\frac{1}{2}\beta_c\delta}.$$

We immediately see that this jump is an explicit function of β_c and therefore a function of $G\rho_F$. In Figure 5 that function is shown. It is seen that the jump gets enhanced when β_c increases ($G\rho_F$ decreases). The maximum jump equal 1.5372 is obtained at about $\beta_c = 400$ eV^{-1} what corresponds to $G\rho_F \approx 0.66$. If the BCS coupling constant decreases ($\beta_c \to \infty$) further, the jump tends to the familiar value 1.426... This figure shows some limitations of the conventional BCS theory regarding strong coupling regime. As is known from experiment lead or some high T_c superconductors exhibit larger values of coupling constants and the specific heat jump than the BCS values [20]. Unfortunately, the conventional BCS theory cannot provide a sufficiently good frame for the description of them. When $G\rho_F$ becomes too large, then the jump of the specific heat is too low and the theory fails. Even in our case, where $G\rho_F = 1$, one can notice the onset of this effect and as a consequence the jump equal 1.3826. Thus, a more general theory is needed for the description of strong coupling superconductors. The Eliashberg approach or the concept

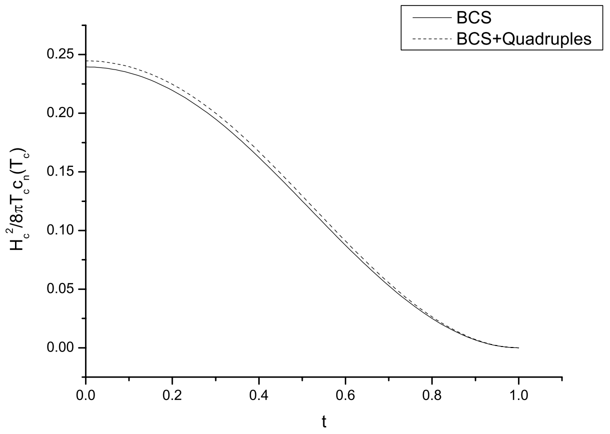

Fig. 6. The squared critical magnetic fields H_c^2 in $8\pi c_n(T_c)T_c$ units are plotted for the pure BCS and mixed states. The continuous curve corresponds to the pure BCS case. The dashed line corresponds to the mixed case. They were calculated according to equations (4.6), (5.3) and (5.4). The curve for the mixed state exceeds that for the pure BCS case.

of tightly bound polarons [20] would be good examples of such theories but the generalization to involve the four-fermion interactions poses a great challenge.

What remains is the squared critical magnetic field. This function is presented in Figure 6 together with the BCS curve. It is seen that the squared critical magnetic field for the mixed state exceeds the BCS one. Both curves exhibit convexity down in the vicinity of the critical temperature. This is connected with the fact that the critical temperature is much higher here than those for superconductors in the weak-coupling regime. This means that such an effect could not be revealed in this limit due to very low temperatures.

At the end of this section we would like to show the analytical expressions for the quadruple gap and the corrections to some thermodynamic functions in the weak-coupling regime. Let us start with the vicinity of $T = 0$. In the paper [20] one can find the following formula for the BCS gap at very low temperatures

$$|\Delta_G(t)| = |\Delta_G(0)| - \sqrt{2\pi\beta_c^{-1}t|\Delta_G(0)|}e^{-|\Delta_G(0)|\beta_c t^{-1}}. \tag{5.13}$$

Because the system is at very low temperatures and $\frac{|\Delta_G(0)|}{\delta} \ll 1$ the expression (5.2) can be approximated by

$$|\Delta_g| \approx \frac{1}{4}g\rho_F|\Delta_G(t)|^2 \int_{-\delta}^{\delta} \frac{d\xi}{E_G^2} \approx \frac{\pi}{4}g\rho_F|\Delta_G(t)|,$$

where at the last stage the approximation $\arctan\frac{\delta}{|\Delta_G(t)|} \approx \frac{\pi}{2}$ was used. Finally, the quadruple gap in the vicinity of $T = 0$ is

$$|\Delta_g| \approx \frac{1}{4}g\rho_F|\Delta_G(0)| - \frac{1}{4}g\rho_F \sqrt{2\pi\beta_c^{-1}t|\Delta_G(0)|}e^{-|\Delta_G(0)|\beta_c t^{-1}}. \tag{5.14}$$

It is easy to show that the corrections to the entropy density and specific heat vanish when $t \to 0$. The correction to the squared critical magnetic field at $T = 0$ is as follows

$$\frac{\Delta H_c^2(0)}{8\pi c_n(T_c)T_c} \approx \frac{3}{32}\beta_c^2 g\rho_F|\Delta_G(0)|^2$$

and is in agreement with the result from Section 4.

Now, we proceed towards the opposite limit $T \to T_c$. In the paper [20] the relationship $\frac{\tanh x}{x} = \sum_{n=-\infty}^{\infty}\frac{1}{x^2+(\pi(n+\frac{1}{2}))^2}$, where n is integer, was applied in order to obtain $|\Delta_G(t)| \approx \pi\beta_c^{-1}\sqrt{\frac{8}{7\zeta(3)}}t\sqrt{1-t}$, where $\zeta(3)$ is the Riemann Zeta function. Since the temperature is very close to $t = 1$ this formula is usually approximated by $|\Delta_G(t)| \approx \pi\beta_c^{-1}\sqrt{\frac{8}{7\zeta(3)}}\sqrt{1-t}$. It is reasonable to follow this route and use in (5.2)

$$\left(\frac{\tanh x}{x}\right)^2 = \sum_{\substack{n=-\infty\\ m=-\infty}}^{\infty} \frac{1}{x^2+(\pi(n+\frac{1}{2}))^2}\frac{1}{x^2+(\pi(m+\frac{1}{2}))^2}.$$

After performing the integration and a few steps we obtain finally

$$|\Delta_g(t)| \approx \frac{2}{\pi^2}\beta_c t^{-1} g\rho_F|\Delta_G(t)|^2 \times \sum_{\substack{n=0\\ m=0}}^{\infty}\frac{1}{(2n+1)(2m+1)(n+m+1)}.$$

The sum in the expression above is approximately equal 2.104 hence after making use of the more accurate form of $|\Delta_G(t)|$ it yields

$$|\Delta_g(t)| \approx 4.208\ \beta_c^{-1} g\rho_F\frac{8}{7\zeta(3)}(1-t)t \approx 4.208\ \beta_c^{-1} g\rho_F\frac{8}{7\zeta(3)}(1-t). \tag{5.15}$$

It is immediately visible that the quadruple gap is a linear function of t in the vicinity of T_c. Having found $|\Delta_g(t)|$ we are able to write the corrections to the rest of the thermodynamic functions down. Let us start with the correction to the squared critical field, namely

$$\frac{\Delta H_c^2(t)}{8\pi c_n(T_c)T_c} \approx 26.561\ g\rho_F\left(\frac{8}{7\zeta(3)}\right)^2(1-t)^2, \tag{5.16}$$

It is worthwhile to note that the squared critical field in the BCS theory is proportional to $(1-t)^2$ [18] in the vicinity of T_c that is very low in the weak-coupling regime. The correction to the entropy density reads

$$\frac{\Delta s(t)}{c_n(T_c)} \approx -53.122\ \frac{g\rho_F}{\pi^2}\left(\frac{8}{7\zeta(3)}\right)^2(1-t) \tag{5.17}$$

and finally the correction to the specific heat is

$$\frac{\Delta c(t)}{c_n(T_c)} \approx 53.122\frac{g\rho_F}{\pi^2}\left(\frac{8}{7\zeta(3)}\right)^2 t \qquad (5.18)$$

that leads to the jump with respect to the BCS result

$$\left.\frac{\Delta c}{c_n(T_c)}\right|_{T=T_c} \approx 53.122\frac{g\rho_F}{\pi^2}\left(\frac{8}{7\zeta(3)}\right)^2. \qquad (5.19)$$

The very interesting question arises if there is a link between equations (5.11) and (5.19). It turns out that for the set of parameters used in the paper the formula (5.19) gives 0.2432 what significantly exceeds the value 0.0975 and obviously overestimates the value of the jump. The agreement is obtained when the BCS coupling is sufficiently weak and as a consequence β_c is very large. Let us take (5.12) for some very large β_c and t equal 1 and as a result very large c_0. It yields

$$|\Delta_G|\frac{d|\Delta_G|}{dt} \approx -\frac{4}{c_0\beta_c},$$

then let us substitute the expression above to (5.11). One obtains

$$\left.\frac{\Delta c}{c_n(T_c)}\right|_{T=T_c} \approx \frac{48}{\pi^2}g\rho_F. \qquad (5.20)$$

For instance, if $g\rho_F = 0.005$ then equations (5.19) and (5.20) yield 0.02423. As is seen all the corrections are linear in $g\rho_F$. This linearity implies non-universality of the corrections.

6 The mean field approach

In this section we would like to show strong connections with the results obtained in [10]. In that paper we tried to address the problem of thermodynamics of the general Hamiltonian H defined in the Introduction. The mean field method was used in order to obtain the statistical sum and two orders parameters - for Cooper's pairs and quadruples, respectively. Both gaps were assumed to be real. Unfortunately, the final expressions turned out to be very complicated. Let us generalize the problem to the case with two complex gaps. Our mean field Hamiltonian reads

$$H_M = \sum_{\mathbf{k}>\mathbf{0}} H_{M\mathbf{k}} = \sum_{\mathbf{k}>\mathbf{0}} (\xi_{\mathbf{k}} \sum_{\sigma}(n_{\mathbf{k}\sigma}+n_{-\mathbf{k}\sigma}) - \Delta_{G\mathbf{k}}(\alpha^*_{\mathbf{k}}+\alpha^*_{-\mathbf{k}})$$
$$- \Delta^*_{G\mathbf{k}}(\alpha_{\mathbf{k}}+\alpha_{-\mathbf{k}}) - 2\Delta^*_{g\mathbf{k}}\beta_{\mathbf{k}} - 2\Delta_{g\mathbf{k}}\beta^*_{\mathbf{k}} + C_{\mathbf{k}}), \qquad (6.1)$$

where

$$\alpha_{\mathbf{k}} = a_{-\mathbf{k}-}a_{\mathbf{k}+}, \quad \beta_{\mathbf{k}} = b_{-\mathbf{k}}b_{\mathbf{k}}$$

$$C_{\mathbf{k}} = \Delta_{G\mathbf{k}}\sigma^*_{\mathbf{k}} + \Delta^*_{G\mathbf{k}}\sigma_{\mathbf{k}} + \Delta_{g\mathbf{k}}\tau^*_{\mathbf{k}} + \Delta^*_{g\mathbf{k}}\tau_{\mathbf{k}}$$

$$\Delta_{G\underline{p}} := |\Lambda|^{-1}\sum_{\underline{p}'} G_{\mathbf{k}\mathbf{k}'}\sigma_{\mathbf{k}'}, \quad \Delta_{g\mathbf{k}} := |\Lambda|^{-1}\sum_{\underline{p}'} g_{\mathbf{k}\mathbf{k}'}\tau_{\mathbf{k}'} \qquad (6.2)$$

with $\sigma_{G\mathbf{k}} = \frac{\mathrm{Tr}\, e^{-\beta H_{M\mathbf{k}}}\alpha_{\mathbf{k}}}{\mathrm{Tr}\, e^{-\beta H_{M\mathbf{k}}}}$ and $\tau_{g\mathbf{k}} = \frac{\mathrm{Tr}\, e^{-\beta H_{M\mathbf{k}}}\beta_{\mathbf{k}}}{\mathrm{Tr}\, e^{-\beta H_{M\mathbf{k}}}}$ in practice. We followed the standard procedure of Bogolyubov et al. [14,15] and the method of Czerwonko [16,17] for the diagonalization of the Hamiltonian $H_{M\mathbf{k}}$. Due to the lack of space the reader is referred to [10], where the details of the procedures can be found.

The result of these methods is as follows:

(A) There are four 1-dimensional and four 2-dimensional eigenspaces $M_{\mathbf{k}i}(i = 1,2,3,4,5,6,7,8)$ of the $H_{M\mathbf{k}}$. They are spanned, respectively, by the following vectors with the corresponding eigenvalues $E_{\mathbf{k}}$ and $E_{\mathbf{k}\pm}$ equal as follows:

1.	$\vert 1010\rangle$	$E_{\mathbf{k}} = 2\xi_{\mathbf{k}}$	5.	$\vert 1000\rangle$	$\vert 1110\rangle$	$E_{\mathbf{k}\pm}$
2.	$\vert 0101\rangle$	$E_{\mathbf{k}} = 2\xi_{\mathbf{k}}$	6.	$\vert 0001\rangle$	$\vert 0111\rangle$	$E_{\mathbf{k}\pm}$
3.	$\vert 1100\rangle$	$E_{\mathbf{k}} = 2\xi_{\mathbf{k}}$	7.	$\vert 0010\rangle$	$\vert 1011\rangle$	$E_{\mathbf{k}\pm}$
4.	$\vert 0011\rangle$	$E_{\mathbf{k}} = 2\xi_{\mathbf{k}}$	8.	$\vert 0100\rangle$	$\vert 1101\rangle$	$E_{\mathbf{k}\pm}$

where $E_{\mathbf{k}\pm} = 2\xi_{\mathbf{k}} \pm E_{G\mathbf{k}}$ with $E_{G\mathbf{k}} = (\xi^2_{\mathbf{k}} + |\Delta_{G\mathbf{k}}|^2)^{1/2}$. In each of the subspaces $M_{\mathbf{k}i}(i = 5,6,7,8)$ the eigenproblem of $H_{M\mathbf{k}}$ reduces to that of the matrix

$$\begin{pmatrix} \xi_{\mathbf{k}} & \Delta^*_{G\mathbf{k}} \\ \Delta_{G\mathbf{k}} & 3\xi_{\mathbf{k}} \end{pmatrix}. \qquad (6.3)$$

The eigenvectors of $H_{M\mathbf{k}}$ in these subspaces have the form

$$|E_{\mathbf{k}\pm}\rangle = c_{\mathbf{k}\pm}|n_1n_2n_3n_4\rangle + d_{\mathbf{k}\pm}|m_1m_2m_3m_4\rangle \qquad (6.4)$$

where $\sum_{i=1}^4 n_i = 1$, $\sum_{i=1}^4 m_i = 3$ and

$$|c_{\mathbf{k}\pm}|^2 = \frac{(\xi_{\mathbf{k}} \mp E_{G\mathbf{k}})^2}{|\Delta_{G\mathbf{k}}|^2 + (\xi_{\mathbf{k}} \mp E_{G\mathbf{k}})^2},$$
$$|d_{\mathbf{k}\pm}|^2 = \frac{|\Delta_{G\mathbf{k}}|^2}{|\Delta_{G\mathbf{k}}|^2 + (\xi_{\mathbf{k}} \mp E_{G\mathbf{k}})^2}.$$

(B) There is one 4-dimensional common subspace $M_{\mathbf{k}9}$ of $H_{M\mathbf{k}}$ spanned by the vectors $|0000\rangle$, $|1001\rangle$, $|0110\rangle$, $|1111\rangle$. Let us use the following basis in $M_{\mathbf{k}9}$:

$$\{|0000\rangle, -|1001\rangle, |0110\rangle, -|1111\rangle\} \qquad (6.5)$$

and denote the projector on $M_{\mathbf{k}9}$ by $P_{\mathbf{k}9}$. Therefore, in the basis (6.5) we have

$$P_{\mathbf{k}9}H_{\mathbf{k}}P_{\mathbf{k}9} = \begin{pmatrix} 0 & \Delta^*_{G\mathbf{k}} & \Delta^*_{G\mathbf{k}} & 2\Delta^*_{g\mathbf{k}} \\ \Delta_{G\mathbf{k}} & 2\xi_{\mathbf{k}} & 0 & \Delta^*_{G\mathbf{k}} \\ \Delta_{G\mathbf{k}} & 0 & 2\xi_{\mathbf{k}} & \Delta^*_{G\mathbf{k}} \\ 2\Delta_{g\mathbf{k}} & \Delta_{G\mathbf{k}} & \Delta_{G\mathbf{k}} & 4\xi_{\mathbf{k}} \end{pmatrix}. \qquad (6.6)$$

Consecutively, the index $\mathbf{k}$ will be suppressed in this section. The solutions of the eigenproblem are:

$$E^{(2)} = 2\xi$$

and

$$E^{(k)} = 2\xi + y_k, \tag{6.7}$$

where

$$y_k = 2(-1)^k\sqrt{r}\cos\left(\frac{\varphi}{3} + \frac{k\pi}{3}\right),\ k = 0, \pm 1 \tag{6.8}$$

with $r = 4/3(|\Delta_g|^2 + |\Delta_G|^2 + \xi^2)$, $\cos\varphi = tr^{-\frac{3}{2}}$ and $t = 2(\Delta_g\Delta_G^*\Delta_G^* + \Delta_g^*\Delta_G\Delta_G)$. These solutions yield the corresponding eigenvalues of $H_{M\mathbf{k}}$ in $M_{\mathbf{k9}}$, viz., Let $u^{(j)}$, $v_1^{(j)}$, $v_2^{(j)}$, $s^{(j)}$ denote the components of the eigenvectors $|E^{(j)}\rangle$ of P_9HP_9 in the basis (6.5):

$$P_9HP_9|E^{(j)}\rangle = E^{(j)}|E^{(j)}\rangle \tag{6.9}$$

along with

$$|E^{(j)}\rangle = u^{(j)}|0000\rangle - v_1^{(j)}|1001\rangle + v_2^{(j)}|0110\rangle - s^{(j)}|1111\rangle,\ j = 0, \pm 1, 2. \tag{6.10}$$

One finds

$$|E^{(2)}\rangle = |2\xi\rangle = \frac{1}{\sqrt{2}}(|1001\rangle + |0110\rangle)$$

and the components of the remaining three eigenvectors $|E^{(j)}\rangle$ equal

$$|u^{(j)}|^2 = \frac{|a^{(j)}|^2}{D^{(j)}},\ v_1^{(j)} = v_2^{(j)},\ |v_1^{(j)}|^2 = \frac{|b^{(j)}|^2}{D^{(j)}},\ |s^{(j)}|^2 = \frac{|c^{(j)}|^2}{D^{(j)}}, = 0 \pm 1 \tag{6.11}$$

where

$$|a^{(i)}|^2 = (2\Delta_g^*\Delta_G - (4\xi - E^{(i)})\Delta_G^*)(2\Delta_g\Delta_G^* - (4\xi - E^{(i)})\Delta_G)(E^{(i)} - 2\xi)^2, \tag{6.12}$$

$$|b^{(i)}|^2 = 4(\Delta_g^*\Delta_G\Delta_G + \Delta_g\Delta_G^*\Delta_G^* + |\Delta_G|^2(E^{(i)} - 2\xi))^2, \tag{6.13}$$

$$|c^{(i)}|^2 = (E^{(i)}\Delta_G + 2\Delta_g\Delta_G^*)(E^{(i)}\Delta_G^* + 2\Delta_g^*\Delta_G)(E^{(i)} - 2\xi)^2, \tag{6.14}$$

$$D^{(i)} = |a^{(i)}|^2 + 2|b^{(i)}|^2 + |c^{(i)}|^2. \tag{6.15}$$

7 Connection with the mean field approach

We would like to show that there exists the link between these both approaches to the problem of the coexistence of Cooper's pairs and quadruples. The simplest way to do this is to restrict oneself to the ground state. We are still interested in the case in which $\frac{g\rho_F}{G\rho_F} \ll 1$. Then, $E^{(-1)}$ is connected with the energy of the ground state. For $i = -1$ one finds that

$$\varphi = \arccos 2\left(\frac{3}{4}\right)^{3/2}\frac{\Delta_g^*\Delta_G\Delta_G + \Delta_g\Delta_G^*\Delta_G^*}{(|\Delta_g|^2 + |\Delta_G|^2 + \xi^2)^{3/2}}.$$

It is easy to show that in this regime of coupling constants we have

$$2\left(\frac{3}{4}\right)^{3/2}\frac{\Delta_g^*\Delta_G\Delta_G + \Delta_g\Delta_G^*\Delta_G^*}{(|\Delta_g|^2 + |\Delta_G|^2 + \xi^2)^{3/2}} \ll 1$$

and the following approximation is valid

$$\frac{\varphi}{3} \approx \frac{\pi}{6} - \frac{1}{2}\frac{\sqrt{3}}{2}\frac{\Delta_g^*\Delta_G\Delta_G + \Delta_g\Delta_G^*\Delta_G^*}{(|\Delta_g|^2 + |\Delta_G|^2 + \xi^2)^{3/2}}.$$

Making use of the expression above we obtain

$$\cos\left(\frac{\varphi}{3} - \frac{\pi}{3}\right) = \cos\left(\frac{\pi}{6} + \frac{1}{2}\frac{\sqrt{3}}{2}\frac{\Delta_g^*\Delta_G\Delta_G + \Delta_g\Delta_G^*\Delta_G^*}{(|\Delta_g|^2 + |\Delta_G|^2 + \xi^2)^{3/2}}\right) \approx \frac{\sqrt{3}}{2} - \frac{\sqrt{3}}{8}\frac{\Delta_g^*\Delta_G\Delta_G + \Delta_g\Delta_G^*\Delta_G^*}{(|\Delta_g|^2 + |\Delta_G|^2 + \xi^2)^{3/2}}.$$

Finally, we are able to write down the energy $E^{(-1)}$, viz.,

$$E^{(-1)} = 2\xi - 2\sqrt{|\Delta_g|^2 + |\Delta_G|^2 + \xi^2} + \frac{1}{2}\frac{\Delta_g^*\Delta_G\Delta_G + \Delta_g\Delta_G^*\Delta_G^*}{|\Delta_g|^2 + |\Delta_G|^2 + \xi^2} \tag{7.1}$$

and the remaining energies

$$E^{(1)} = 2\xi - \frac{\Delta_g^*\Delta_G\Delta_G + \Delta_g\Delta_G^*\Delta_G^*}{|\Delta_g|^2 + |\Delta_G|^2 + \xi^2},$$

$$E^{(0)} = 2\xi + 2\sqrt{|\Delta_g|^2 + |\Delta_G|^2 + \xi^2} + \frac{1}{2}\frac{\Delta_g^*\Delta_G\Delta_G + \Delta_g\Delta_G^*\Delta_G^*}{|\Delta_g|^2 + |\Delta_G|^2 + \xi^2}.$$

As one can see, the lowest energy corresponds to $E^{(-1)}$. In order to obtain the full ground state energy it is advisable to write down the free energy of the system, viz.,

$$F = -\beta^{-1}\ln\prod_{\mathbf{k}>0} Z_{\mathbf{k}}, \tag{7.2}$$

where the statistical sum $Z_{\mathbf{k}}$ is

$$Z_{\mathbf{k}} = e^{-\beta(2\xi_k + \Delta_{G\mathbf{k}}\sigma_{\mathbf{k}}^* + \Delta_{G\mathbf{k}}^*\sigma_{\mathbf{k}} + \Delta_{g\mathbf{k}}\tau_{\mathbf{k}}^* + \Delta_{g\mathbf{k}}^*\tau_{\mathbf{k}})} \times (5 + 4e^{-\beta E_{G\mathbf{k}}} + 4e^{\beta E_{G\mathbf{k}}} + e^{-\beta y_{-1\mathbf{k}}} + e^{-\beta y_{1\mathbf{k}}} + e^{-\beta y_{0\mathbf{k}}}).$$

In $\beta \to \infty$ limit we obtain the ground state energy

$$E_0 = \sum_{\mathbf{k}>0}(2\xi_k + \Delta_{G\mathbf{k}}\sigma_{\mathbf{k}}^* + \Delta_{G\mathbf{k}}^*\sigma_{\mathbf{k}} + \Delta_{g\mathbf{k}}\tau_{\mathbf{k}}^* + \Delta_{g\mathbf{k}}^*\tau_{\mathbf{k}} + y_{-1\mathbf{k}}),$$

what can be transformed to

$$E_0 = \sum_{\mathbf{k}>0}\left(2\xi_k - 2\sqrt{|\Delta_{g\mathbf{k}}|^2 + |\Delta_{G\mathbf{k}}|^2 + \xi^2} + \frac{1}{2}\frac{\Delta_{g\mathbf{k}}^*\Delta_{G\mathbf{k}}\Delta_{G\mathbf{k}} + \Delta_{g\mathbf{k}}\Delta_{G\mathbf{k}}^*\Delta_{G\mathbf{k}}^*}{|\Delta_{g\mathbf{k}}|^2 + |\Delta_{G\mathbf{k}}|^2 + \xi^2} + \Delta_{G\mathbf{k}}\sigma_{\mathbf{k}}^* + \Delta_{G\mathbf{k}}^*\sigma_{\mathbf{k}} + \Delta_{g\mathbf{k}}\tau_{\mathbf{k}}^* + \Delta_{g\mathbf{k}}^*\tau_{\mathbf{k}}.\right)$$

Now if we use the following limits

$$\lim_{\substack{\beta\to\infty\\ \Delta_{g\mathbf{k}}\to 0}} \sigma_{\mathbf{k}} = -\lim_{\Delta_{g\mathbf{k}}\to 0}(u_{\mathbf{k}}^{(-1)*}v_{1\mathbf{k}}^{(-1)} + v_{1\mathbf{k}}^{(-1)*}s_{\mathbf{k}}^{(-1)})$$

$$= u_{\mathbf{k}}^{*}v_{\mathbf{k}} = \frac{\Delta_{G\mathbf{k}}}{2E_{G\mathbf{k}}}, \tag{7.3}$$

$$\lim_{\substack{\beta\to\infty\\ \Delta_{g\mathbf{k}}\to 0}} \tau_{\mathbf{k}} = -\lim_{\Delta_{g\mathbf{k}}\to 0} u_{\mathbf{k}}^{(-1)*}s_{\mathbf{k}}^{(-1)}$$

$$= -(u_{\mathbf{k}}^{*}v_{\mathbf{k}})^2 = -\frac{\Delta_{G\mathbf{k}}\Delta_{G\mathbf{k}}}{4E_{G\mathbf{k}}^2} \tag{7.4}$$

along with the corresponding ones for the complex conjugates and the following approximation

$$\sqrt{|\Delta_{g\mathbf{k}}|^2 + |\Delta_{G\mathbf{k}}|^2 + \xi^2} \approx E_{G\mathbf{k}},$$

we obtain exactly the same expression for the ground state like equation (2.6). Moreover, we obtain the same equations for the order parameters. To see this it suffices to substitute the limits (7.3) and (7.4) to the definitions (6.2).

One important remark should be made. The mean field theory points to some restrictions of the perturbative approach. In the latter the BCS order parameter is not directly influenced by quadruples while in the former this influence emerges in the natural way. In order to incorporate this influence into perturbation theory one would have to determine the first order correction to the BCS ground state vector (2.1) and calculate the total ground state energy for the full Hamiltonian H with respect to the improved ground state vector. However, this procedure seems to be much more complicated in practice than the Bogolyubov's approach. In fact, in the mean field theory both parameters are coupled from the very beginning what can be seen from the following expansions for small $\Delta_{g\mathbf{k}}$ and $\Delta_{g\mathbf{k}}^*$

$$\sigma_{\mathbf{k}} = \frac{1}{2}\frac{\Delta_{G\mathbf{k}}}{E_{G\mathbf{k}}} - \Delta_{G\mathbf{k}}^*\frac{\xi_k^2 + E_{G\mathbf{k}}^2}{4E_{G\mathbf{k}}^4}\Delta_{g\mathbf{k}} + \frac{\Delta_{G\mathbf{k}}^3}{4E_{G\mathbf{k}}^4}\Delta_{g\mathbf{k}}^* + \ldots \tag{7.5}$$

$$\tau_{\mathbf{k}} = -\frac{1}{4}\frac{\Delta_{G\mathbf{k}}^2}{E_{G\mathbf{k}}^2} + \frac{-3|\Delta_{G\mathbf{k}}|^2 + 8E_{G\mathbf{k}}^4}{16E_{G\mathbf{k}}^5}\Delta_{g\mathbf{k}} - \frac{3\Delta_{G\mathbf{k}}^4}{16E_{G\mathbf{k}}^5}\Delta_{g\mathbf{k}}^* + \ldots \tag{7.6}$$

It is not difficult to show that for the parameters used in Section 5 and the assumptions $\frac{|\Delta_g|}{E_G} \ll 1$, $\frac{|\Delta_G|}{E_G} \leq 1$, $\frac{|\xi|}{E_G} \leq 1$ one can neglect linear corrections and the subsequent terms because they are small when compared with the zero order term (index $\mathbf{k}$ has been dropped). For linear terms in the expansion for σ we have

$$\frac{|\Delta_g|}{E_G}\frac{|\Delta_G|}{E_G}\frac{\xi^2 + E_G^2}{4E_G^2} \leq \frac{1}{2}\frac{|\Delta_g|}{E_G}\frac{|\Delta_g|}{E_G} \ll \frac{1}{2}\frac{|\Delta_G|}{E_G}$$

and

$$\frac{|\Delta_g|}{E_G}\frac{|\Delta_G|^3}{4E_G^3} \ll \frac{1}{2}\frac{|\Delta_G|}{E_G} \Leftrightarrow \frac{1}{2}\frac{|\Delta_g|}{E_G}\frac{|\Delta_G|^2}{E_G^2} \ll 1,$$

whereas for τ

$$\frac{3}{16}\frac{|\Delta_G|^4}{E_G^4}\frac{|\Delta_g|}{E_G} \ll \frac{1}{4}\frac{|\Delta_G|^2}{E_G^2} \Leftrightarrow \frac{3}{4}\frac{|\Delta_G|^2}{E_G^2}\frac{|\Delta_g|}{E_G} \ll 1,$$

$$\frac{8}{16}\frac{|\Delta_g|}{E_G} \ll \frac{1}{4}\frac{|\Delta_G|^2}{E_G^2} \Leftrightarrow 2\frac{|\Delta_g|}{|\Delta_G|} \ll \frac{|\Delta_G|}{E_G}.$$

The last inequality holds for the parameters used in this paper because the right hand side of the inequality above is larger by one order of magnitude than the left hand side. Of course, in more general approach to the problem one has to include at least the first order corrections in the equations for the order parameters what leads to solving the system of four equations. The situation becomes much more complicated at finite temperatures but it is still possible to obtain the agreement with results coming from perturbation theory. It means that the form of the gap equations after keeping only zero order terms in the expansions with respect to Δ_g and Δ_g^* are the same at finite temperatures as it is in perturbation theory. The same assertion concerns the free energy.

In the mean field approach the necessity of introducing the complex order parameters is transparent. If we admitted them to be real we would get into some problems with the definition and interpretation of the quadruple gap due to the negative sign in front of the zero order term. Such a definition would lead to the negative gap. Even if the quadruple gap was negative we would still obtain the negative correction to the BCS ground state energy and as a result the state with lower energy than BCS one.

8 Conclusions

The BCS system with a four-fermion interaction was investigated. This was done by using perturbation theory with the BCS system standing for an unperturbed one. The ground state and thermodynamic properties were examined up to the first order of the perturbation expansion. As a result, the total ground state energy of the system turned out to be lower than the BCS one. Moreover, both interactions together do not shift the chemical potential with respect to the Fermi energy of the free electron gas. The resulting complex gap for quadruples is determined by the BCS complex gap and vanishes when the BCS gap becomes zero. The thermodynamics of the total system differs slightly from the BCS thermodynamics. For example, the squared critical magnetic field exceeds that for the BCS system. The higher jump than that in the BCS system occurs. It is supposed here that the second order corrections are not important at finite temperatures because they are not greater than 0.5 percent of the first order correction in the ground state. The analytical expressions for the quadruple gap and the corrections to the thermodynamic functions in the vicinity of $T = 0$ and $T = T_c$ were found as well. This concerns the weak-coupling regime only and all the expressions exhibit non-universality due to their linear dependence on $g\rho_F$.

Moreover, we confronted our results with those obtained in [10]. It was explicitly done for the ground state only but the same conclusions are valid for the expressions at finite temperatures as well. We showed the agreement between both methods, it is, the same expressions for the ground state energy, the same equations for the gap parameters (with neglecting the corrections). However, perturbation theory is restricted only to the case when the four-fermion interaction is significantly weaker than BCS interaction. For instance, the effect of quadruples on the BCS gap parameter is not present at this stage in the paper unless one incorporates the first order correction to the BCS ground state vector. Yet in the case of the very weak four-fermion interaction with respect to the BCS one such an effect is not relevant. The mean field approach is independent of how strong is the four-fermion interaction with respect to BCS one. Finally, our results obtained by using perturbation theory show some tendencies in behavior of the thermodynamic functions. The effects are not very strong, especially in the weak-coupling regime, and only the measuring the magnetic flux can provide the ultimate answer regarding the presence of quadruples in the system.

Author would like to thank Dr. Kristian K. Müller-Nedebock for fruitful and helpful discussions and suggestions.

Appendix A

Let us introduce a new notation for vectors spanning the subspace of $\mathbf{k}>0$, namely

$$|n_1n_2n_3n_4\rangle := (\alpha^*_{\mathbf{k}1})^{n_1}(\alpha^*_{\mathbf{k}2})^{n_2}(\alpha^*_{\mathbf{k}3})^{n_3}(\alpha^*_{\mathbf{k}4})^{n_4}|0\rangle\,,$$

where $n_i = 0,1,\ i=1,2,3,4$. Thus the normalized $\mathbf{k}$-excited states in terms of that notation are represented by the vectors

$$|\mathbf{k}1\rangle := \alpha^*_{\mathbf{k}1}|\mathbf{k}BCS\rangle = u_{\mathbf{k}}|1000\rangle - v_{\mathbf{k}}|1110\rangle, \quad (A.1)$$

$$|\mathbf{k}2\rangle := \alpha^*_{\mathbf{k}2}|\mathbf{k}BCS\rangle = u_{\mathbf{k}}|0100\rangle - v_{\mathbf{k}}|1101\rangle, \quad (A.2)$$

$$|\mathbf{k}3\rangle := \alpha^*_{\mathbf{k}3}|\mathbf{k}BCS\rangle = u_{\mathbf{k}}|0010\rangle - v_{\mathbf{k}}|1011\rangle, \quad (A.3)$$

$$|\mathbf{k}4\rangle := \alpha^*_{\mathbf{k}4}|\mathbf{k}BCS\rangle = u_{\mathbf{k}}|0001\rangle - v_{\mathbf{k}}|0111\rangle, \quad (A.4)$$

$$|\mathbf{k}12\rangle := \alpha^*_{\mathbf{k}1}\alpha^*_{\mathbf{k}2}|\mathbf{k}BCS\rangle = |1100\rangle, \quad (A.5)$$

$$|\mathbf{k}13\rangle := \alpha^*_{\mathbf{k}1}\alpha^*_{\mathbf{k}3}|\mathbf{k}BCS\rangle = |1010\rangle, \quad (A.6)$$

$$|\mathbf{k}14\rangle := \alpha^*_{\mathbf{k}1}\alpha^*_{\mathbf{k}4}|\mathbf{k}BCS\rangle = -u_{\mathbf{k}}v_{\mathbf{k}}|0000\rangle + v^2_{\mathbf{k}}|0110\rangle + u^2_{\mathbf{k}}|1001\rangle - u_{\mathbf{k}}v_{\mathbf{k}}|1111\rangle, \quad (A.7)$$

$$|\mathbf{k}23\rangle := \alpha^*_{\mathbf{k}2}\alpha^*_{\mathbf{k}3}|\mathbf{k}BCS\rangle = u_{\mathbf{k}}v_{\mathbf{k}}|0000\rangle + u^2_{\mathbf{k}}|0110\rangle + v^2_{\mathbf{k}}|1001\rangle + u_{\mathbf{k}}v_{\mathbf{k}}|1111\rangle, \quad (A.8)$$

$$|\mathbf{k}24\rangle := \alpha^*_{\mathbf{k}2}\alpha^*_{\mathbf{k}4}|\mathbf{k}BCS\rangle = |0101\rangle, \quad (A.9)$$

$$|\mathbf{k}34\rangle := \alpha^*_{\mathbf{k}3}\alpha^*_{\mathbf{k}4}|\mathbf{k}BCS\rangle = |0011\rangle, \quad (A.10)$$

$$|\mathbf{k}123\rangle := \alpha^*_{\mathbf{k}1}\alpha^*_{\mathbf{k}2}\alpha^*_{\mathbf{k}3}|BCS_{\mathbf{k}}\rangle_{\mathbf{k}} = v_{\mathbf{k}}|1000\rangle + u_{\mathbf{k}}|1110\rangle, \quad (A.11)$$

$$|\mathbf{k}124\rangle := \alpha^*_{\mathbf{k}1}\alpha^*_{\mathbf{k}2}\alpha^*_{\mathbf{k}4}|BCS_{\mathbf{k}}\rangle_{\mathbf{k}} = v_{\mathbf{k}}|0100\rangle + u_{\mathbf{k}}|1101\rangle, \quad (A.12)$$

$$|\mathbf{k}134\rangle := \alpha^*_{\mathbf{k}1}\alpha^*_{\mathbf{k}3}\alpha^*_{\mathbf{k}4}|BCS_{\mathbf{k}}\rangle_{\mathbf{k}} = v_{\mathbf{k}}|0010\rangle + u_{\mathbf{k}}|1011\rangle, \quad (A.13)$$

$$|\mathbf{k}234\rangle := \alpha^*_{\mathbf{k}2}\alpha^*_{\mathbf{k}3}\alpha^*_{\mathbf{k}4}|BCS_{\mathbf{k}}\rangle_{\mathbf{k}} = v_{\mathbf{k}}|0001\rangle + u_{\mathbf{k}}|0111\rangle, \quad (A.14)$$

$$|\mathbf{k}1234\rangle := \alpha^*_{\mathbf{k}1}\alpha^*_{\mathbf{k}2}\alpha^*_{\mathbf{k}3}\alpha^*_{\mathbf{k}4}|BCS\rangle_{\mathbf{k}} = -v^2_{\mathbf{k}}|0000\rangle - v_{\mathbf{k}}u_{\mathbf{k}}|0110\rangle + v_{\mathbf{k}}u_{\mathbf{k}}|1001\rangle + u^2_{\mathbf{k}}|1111\rangle. \quad (A.15)$$

The product $\prod_{\substack{\mathbf{k}':\mathbf{k}'>0\\ \mathbf{k}'\neq\mathbf{k}}}|\mathbf{k}'BCS\rangle$ has been dropped in the expressions (A.1)–(A.15). The spectrum above is the BCS excitation spectrum written in $\mathbf{k}>0$-representation which is more useful for our considerations than that for $\mathbf{k}$ belonging to whole momentum space [2,12].

Appendix B

In this Appendix we would like to show some very important derivatives that are frequently used in the paper. The first is

$$\frac{d|\Delta_g|}{dt} = 2|\Delta_G|\frac{d|\Delta_G|}{dt} + \frac{1}{2}g\rho_F|\Delta_G|^2\frac{d}{dt} \times \int_0^\delta d\xi\left(\frac{\tanh\frac{1}{2}\beta_c t^{-1}E_G}{E_G}\right)^2,$$

where

$$\frac{d}{dt}\int_0^\delta d\xi\left(\frac{\tanh\frac{1}{2}\beta_c t^{-1}E_G}{E_G}\right)^2 = \beta_c t^{-1}|\Delta_G|\frac{d|\Delta_G|}{dt} \times \int_0^\delta \frac{d\xi}{E_G^3}\frac{\tanh\frac{1}{2}\beta_c t^{-1}E_G}{\cosh^2\frac{1}{2}\beta_c t^{-1}E_G} - \beta_c t^{-2}\int_0^\delta\frac{d\xi}{E_G}\frac{\tanh\frac{1}{2}\beta_c t^{-1}E_G}{\cosh^2\frac{1}{2}\beta_c t^{-1}E_G} - 2|\Delta_G|\frac{d|\Delta_G|}{dt}\int_0^\delta\frac{d\xi}{E_G^4}\tanh^2\frac{1}{2}\beta_c t^{-1}E_G.$$

The following derivative is needed for the calculation of the correction to the entropy density

$$\frac{d|\Delta_G|}{dt} = -\frac{\frac{\partial F(t,|\Delta_G|)}{\partial t}}{\frac{\partial F(t,|\Delta_G|)}{\partial|\Delta_G|}} = \frac{1}{2}\beta_c t^{-2}|\Delta_G|^{-1} \times \frac{\int_0^\delta d\xi(1-\tanh^2\frac{1}{2}\beta_c t^{-1}E_G)}{\frac{1}{2}\beta_c t^{-1}\int_0^\delta d\xi\frac{(1-\tanh^2\frac{1}{2}\beta_c t^{-1}E_G)}{E_G^2} - \int_0^\delta d\xi\frac{\tanh\frac{1}{2}\beta_c t^{-1}E_G}{E_G^3}}, \quad (B.1)$$

where the defining equation is $\frac{1}{G\rho_F} = F(t,|\Delta_G|)$ and $F(t,|\Delta_G|) := \int_0^\delta d\xi\frac{\tanh\frac{1}{2}\beta_c t^{-1}E_G}{E_G}$.

To calculate the correction to the specific heat we need

$$\frac{d^2|\Delta_g|^2}{dt^2} = 2\left(\frac{d|\Delta_g|}{dt}\right)^2 + 2|\Delta_g|\frac{d^2|\Delta_g|}{dt^2}, \quad (B.2)$$

where

$$\frac{d^2|\Delta_g|}{dt^2} = 2\left(\frac{d|\Delta_G|}{dt}\right)^2 \frac{|\Delta_g|}{|\Delta_G|^2} + 2|\Delta_G|\left(\frac{d^2|\Delta_G|}{dt^2}\right)\frac{|\Delta_g|}{|\Delta_G|^2}$$
$$+ 2|\Delta_G|\frac{d|\Delta_G|}{dt}\frac{d|\Delta_g|}{dt}|\Delta_G|^{-2} - 4\left(|\Delta_G|\frac{d|\Delta_G|}{dt}\right)^2 \frac{|\Delta_g|}{|\Delta_G|^4}$$
$$+ g\rho_F|\Delta_G|\frac{d|\Delta_G|}{dt}\frac{d}{dt}\int\limits_0^\delta d\xi\left(\frac{\tanh\frac{1}{2}\beta_c t^{-1}E_G}{E_G}\right)^2$$
$$+ \frac{1}{2}g\rho_F|\Delta_G|^2\frac{d^2}{dt^2}\int\limits_0^\delta d\xi\left(\frac{\tanh\frac{1}{2}\beta_c t^{-1}E_G}{E_G}\right)^2.$$

As one can see there is a need for calculation of $\frac{d^2|\Delta_G|}{dt^2}$ and $\frac{d^2}{dt^2}\int\limits_0^\delta d\xi\left(\frac{\tanh\frac{1}{2}\beta_c t^{-1}E_G}{E_G}\right)^2$, however the calculation of them was omitted in the paper due to the significant length.

The formula (5.11) can be derived if one notices that in the limit $t \to 1$ most of terms in (B.2) vanish and the only nonzero are

$$\left(\frac{d|\Delta_g|}{dt}\right)\Bigg|^2_{T=T_c} + g\rho_F c_0\left(|\Delta_G|\frac{d|\Delta_G|}{dt}\right)\Bigg|_{T=T_c}\frac{d|\Delta_g|}{dt}\Bigg|_{T=T_c}$$
$$- \frac{1}{2}g\rho_F^2 c_0^2\left(\frac{d|\Delta_G|}{dt}|\Delta_G|\right)\Bigg|^2_{T=T_c}$$

that lead finally to (5.11). Regarding (5.12) we have to take a closer look at the integrals in (B.1) in the limit $t \to 1$. It suffices to use the following equalities $\frac{d}{dx}\frac{\tanh ax}{x} = a\frac{1-\tanh^2 ax}{x} - \frac{\tanh ax}{x^2}$ and $\frac{d}{dx}\tanh ax = a(1-\tanh^2 ax)$ and notice that the divergence $\frac{1}{\xi}$ cancels out.

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