Thermodynamics of Crossover from Weak- to Strong-Coupling Superconductivity

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In this paper we study an evolution of low-temperature thermodynamical quantities for an electron gas with a $\delta$-function attraction as the system crosses over from weak-coupling (BCS-type) to strong-coupling (Bose-type) superconductivity in three and two dimensions.

1. INTRODUCTION

Recently there was remarkable progress in the study of the crossover from weak-coupling (BCS) superconductivity to Bose-Einstein condensation (BEC) of tightly bound fermion pairs. Although this crossover was first addressed a long time ago [1], [2], the recent interest in this subject [3], [4] was initiated by suggestions of its relevance to High-Temperature Superconductors [5], [6]. This crossover is a remarkable example of smooth evolution between two very different physical systems. A few of its features are: in the BCS superconductors there is one characteristic temperature $T_c$ where superconductivity disappears due to thermal decomposition of Cooper pairs. In contrast, the “Bose-type” superconductor possesses two characteristic temperatures, namely a critical temperature which in the extreme Bose regime does not depend on coupling strength and a substantially higher temperature of thermal pair decomposition. Also the BCS condensate is characterized by a coherence length which coincides with the size of a Cooper pair whereas in the Bose limit the system possesses two characteristic length scales, namely a coherence length which increases with increasing coupling strength and a Cooper pair size which obviously decreases with increasing coupling strength.

In fact, this crossover is related to many other phenomena in various branches of physics. In particular it was generalized to the Chiral Gross-Neveu (GN) model [7], [8]. This model is considered as a toy model for QCD. There are also numerous ongoing discussions of the possibility of the appearance of a pseudogap phase in the Nambu–Jona-Lasinio (NJL) model [9], [10].

In contrast to the particle physics, in the theory of superconductivity the BCS-BEC crossover has been studied in great detail. However, the main subject of the study was the evolution of critical temperature and non-Fermi–liquid properties above $T_c$. Intuitive clarity of the physical picture of this crossover is obscured by the absence of simple analytical and asymptotic results for many other physical quantities (e.g. for the behavior of thermodynamic functions). The low-temperature asymptotics of thermodynamic functions of a BCS superconductor are well known and can be found in many textbooks. However to the

1 The Gross-Neveu and Nambu–Jona-Lasinio models are models of N-component fermions fields that serve for description of dynamic chiral symmetry breakdown in particle physics. Originally the NJL model was proposed in analogy to BCS theory. The NJL model may be treated by mean-field methods in the regime of large number of colors $N_c$ with $1/N_c$ serving as a small parameter of the problem. However in a real world $N_c = 3$ thus as it is not infinite, the system may possess [e.g. at finite temperature] a fluctuation-driven restoration of the chiral symmetry while preserving nonzero constituent quark mass. This would be a phenomenon similar to the symmetry restoration without pairbreaking in strong coupling or low carrier density superconductors. However in the case of the NJL model there are complications that do not allow this problem to be addressed rigorously by perturbative methods [11], [12]. Thus BCS-BEC crossover in superconductors may in some sense serve as a valuable toy model for QCD.
best of the author’s knowledge there are no analogous expressions published for the thermodynamics of BCS-BEC crossover. This paper is an attempt to fill in this gap.

In the model to be investigated in this paper, the crossover from BCS-type to Bose-type superconductivity takes place either by varying the coupling strength, or by decreasing the carrier density. Asymptotic calculations in the BCS and BEC limits will be performed using the crossover parameter $x_0$ that we adopt from [9]. This parameter is directly related to the ratio of the chemical potential and gap function at zero temperature. It is a monotonic function of coupling strength and carrier density [to be seen in Figs. 1 and 2 in two and three dimensions, respectively]. It is also a direct measure for the scattering length $a_s$ of the electron-electron interaction, at zero temperature in three dimensions [to be seen in Eq. (11)], and of the binding energy of the electron-electron pairs in two dimensions [to be seen in Eq. (13)].

The plan of the paper is following: we start by a brief outlining of the results of Refs. [9], [10] for the gap $\Delta(0)$ and chemical potential at zero temperature in the entire crossover region. These are subsequently extended by equations for the low-temperature ($T/\Delta(T) << 1$) behavior of the gap functions, chemical potential and of thermodynamic functions in two and three dimensions up to the boundaries of the region $-1 < x_0 < 1$.

In appendix we also calculate the evolution of thermodynamic quantities near $T_c$ in weak and moderately strong coupling superconductors where mean-field methods are reliable.

II. THE MODEL

The Hamiltonian of our model is the typical BCS Hamiltonian in $D$ dimensions ($\hbar = 1$)

$$H = \sum_\sigma \int d^D x \psi_\sigma^\dagger(x) \left( -\frac{\nabla^2}{2m} - \mu \right) \psi_\sigma(x) + g \int d^D x \psi_\uparrow^\dagger(x) \psi_\downarrow^\dagger(x) \psi_\downarrow(x) \psi_\uparrow(x),$$

where $\psi_\sigma(x)$ is the Fermi field operator, $\sigma = \uparrow, \downarrow$ denotes the spin components, $m$ is the effective fermionic mass, and $g < 0$ the strength of an attractive potential $g \delta(x - x')$.

The mean-field equations for the gap parameter $\Delta$ and the chemical potential $\mu$ are obtained in the standard way from the equations:

$$-\frac{1}{g} = \frac{1}{V} \sum_\mathbf{k} \frac{1}{2E_\mathbf{k}} \tanh \frac{E_\mathbf{k}}{2T},$$

$$n = \frac{1}{V} \sum_\mathbf{k} \left( 1 - \frac{\xi_\mathbf{k}}{E_\mathbf{k}} \tanh \frac{E_\mathbf{k}}{2T} \right),$$

where the sum runs over all wave vectors $\mathbf{k}$, $N$ is the total number of fermions, $V$ the volume of the system, and $E_\mathbf{k} = \sqrt{\xi_\mathbf{k}^2 + \Delta^2}$ with $\xi_\mathbf{k} = k^2/2m - \mu$ are the energies of single-particle excitations.

Changing the sum over $\mathbf{k}$ to an integral over $\xi$ and over the directions of $\mathbf{k}$, on which the integrand does not depend, we arrive in three dimensions at the gap equation:

$$-\frac{1}{g} = \kappa_3 \int_{-\mu}^{\infty} d\xi \frac{\sqrt{\xi^2 + \mu}}{2\sqrt{\xi^2 + \Delta^2}} \tanh \frac{\sqrt{\xi^2 + \Delta^2}}{2T},$$

where the constant $\kappa_3 = m^{3/2}/\sqrt{2}\pi^2$ has dimension energy$^{-3/2}$/volume. In two-dimensions, the density of states is constant, and the gap equation becomes

$$-\frac{1}{g} = \kappa_2 \int_{-\mu}^{\infty} d\xi \frac{1}{2\sqrt{\xi^2 + \Delta^2}} \tanh \frac{\sqrt{\xi^2 + \Delta^2}}{2T},$$

with a constant $\kappa_2 = m/2\pi$ of dimension energy$^{-1}$/two-volume. In two dimensions, the particle number in Eq. (3) can be integrated with the result:
\[ n = \frac{m}{2\pi} \left\{ \sqrt{\mu^2 + \Delta^2} + \mu + 2T \log \left[ 1 + \exp \left( -\sqrt{\frac{\mu^2 + \Delta^2}{T}} \right) \right] \right\}. \]  

(6)

The \( \delta \)-function potential produces an artificial divergence and requires regularization. A BCS superconductor possesses a natural cutoff supplied by the Debye frequency \( \omega_D \). For the crossover problem to be treated here this is no longer a useful quantity, since in the strong-coupling limit all fermions participate in the interaction, not only those in a thin shell of width \( \omega \) treated here this is no longer a useful quantity, since in the strong-coupling limit all fermions participate in the interaction, not only those in a thin shell of width \( \omega_D \) around the Fermi surface. To be applicable in this regime, we renormalize the gap equation in three dimensions with the help of the experimentally observable \( s \)-wave scattering length \( a_s \), for which the low-energy limit of the two-body scattering process gives an equally divergent expression:

\[ \frac{m}{4\pi a_s} = \frac{1}{g} + \frac{1}{V} \sum_k \frac{m}{k^2}. \]  

(7)

Eliminating \( g \) from (9) and (8) we obtain a renormalized gap equation

\[ -\frac{m}{4\pi a_s} = \frac{1}{V} \sum_k \left[ \frac{1}{2E_k} \tanh \frac{E_k}{2T} \frac{m}{k^2} \right], \]  

(8)

in which \( 1/k_F a_s \) plays the role of a dimensionless coupling constant which monotonically increases from \(-\infty \) to \( \infty \) as the bare coupling constant \( g \) runs from small (BCS limit) to large values (BE limit). This equation is to be solved simultaneously with (3). In the BCS limit, the chemical potential \( \mu \) does not differ much from the Fermi energy \( \epsilon_F \), whereas with increasing interaction strength, the distribution function \( n_k \) broadens and \( \mu \) decreases, and in the BE limit, on the other hand we have tightly bound pairs and nondegenerate fermions with a large negative chemical potential \( |\mu| \gg T \).

In three dimensions at \( T = 0 \), equations (8), (3) were solved analytically in entire crossover region in \( \Delta \) to obtain \( \Delta \) and \( \mu \) as functions of crossover parameter \( 1/k_F a_s \). The results are

\[ \frac{\Delta}{\epsilon_F} = \frac{1}{|x_0 I_1(x_0) + I_2(x_0)|^{2/3}}, \]  

(9)

\[ \frac{\mu}{\epsilon_F} = \frac{\mu}{\Delta} \frac{\epsilon_F}{x_0 I_1(x_0) + I_2(x_0)|^{2/3}}, \]  

(10)

\[ \frac{1}{k_F a_s} = \frac{4}{\pi} \frac{x_0 I_2(x_0) - I_1(x_0)}{|x_0 I_1(x_0) + I_2(x_0)|^{1/3}}, \]  

(11)

with the functions

\[ I_1(x_0) = \int_0^\infty dx \frac{x^2}{(x^4 - 2x^2 + x_0^2 + 1)^{3/2}} = (1 + x_0^2)^{1/4} E\left(\frac{\pi}{2}, \kappa\right) - \frac{1}{4x_0^2(1 + x_0^2)^{1/4}} F\left(\frac{\pi}{2}, \kappa\right), \]

\[ I_2(x_0) = \frac{1}{2} \int_0^\infty dx \frac{(x^4 - 2x_0x^2 + x_0^2 + 1)^{1/2}}{x_0(1 + x_0^2)^{1/4}} F\left(\frac{\pi}{2}, \kappa\right), \]

\[ \kappa^2 = \frac{x_0^2}{(1 + x_0^2)^{1/2}}, x_0 = \frac{\mu}{\Delta}, x_1 = \sqrt{\frac{1 + x_0^2 + x_0}{2}}, \]

where \( E(\frac{\pi}{2}, \kappa) \) and \( F(\frac{\pi}{2}, \kappa) \) are the usual elliptic integrals. The quantities (9) and (10) are plotted as functions of the crossover parameter \( x_0 = \mu/\Delta \) in Fig. 1.
FIG. 1. Gap function $\Delta$ and chemical potential $\mu$ at zero temperature as functions of $x_0 = \mu/\Delta$ in three dimensions.

In two dimensions, a nonzero bound state energy $\epsilon_0$ exists for any coupling strength. The cutoff can therefore be eliminated by subtracting from the two-dimensional zero-temperature gap equation

$$ -\frac{1}{g} = \frac{1}{2V} \sum_k \frac{1}{\sqrt{\xi_k^2 + \Delta^2}} = \frac{m}{4\pi} \int_{-x_0}^{\infty} dz \frac{1}{\sqrt{1 + z^2}}. $$

where $z = k^2/2m\Delta - x_0$, the bound-state equation

$$ -\frac{1}{g} = \frac{1}{V} \sum_k \frac{k^2/m + \epsilon_0}{z} = \frac{m}{2\pi} \int_{-x_0}^{\infty} dz \frac{1}{2z + \epsilon_0/\Delta + 2x_0}. $$

After performing the elementary integrals, one finds : $\epsilon_0/\Delta = \sqrt{1 + x_0^2} - x_0$. From Eq. (11) we see that at zero temperature, gap and chemical potential are related to $x_0$ by

$$ \frac{\Delta}{\epsilon_F} = \frac{2}{x_0 + \sqrt{1 + x_0^2}}, $$

$$ \frac{\mu}{\epsilon_F} = \frac{2x_0}{x_0 + \sqrt{1 + x_0^2}}. $$

The two relations are plotted in Fig. 2. From (14) we find the dependence of the ratio $\epsilon_0/\epsilon_F$ on the crossover parameter $x_0$:

$$ \frac{\epsilon_0}{\epsilon_F} = \frac{2\sqrt{1 + x_0^2} - x_0}{\sqrt{1 + x_0^2} + x_0}. $$
FIG. 2. Gap function $\Delta$ and chemical potential $\mu$ at zero temperature as functions of $x_0$ in two dimensions.

III. THE CROSSOVER FROM BCS TO STRONG-COUPLING SUPERCONDUCTIVITY NEAR ZERO TEMPERATURE

A. The range of validity of mean-field approximation

We have extended the above relations to non-zero temperature in the BCS and BEC limits. We use a mean-field approximation which, in the range of its validity, allows a nice simple description of the crossover. It is known that in BCS limit the mean-field approximation is valid for the description of the entire superconductive region. In fact the system crosses over from BCS to Bose condensate in a very narrow region $-1 < x_0 < 1$ (see e.g. [8]) so the BCS approximation is adequate for description of the entire superconductive region in the range $x_0 > 1$. This is in contrast to BEC limit where the superconductive transition is governed by the thermal excitation of collective modes rather than thermal decomposition of individual particles, the effect which is missed in the mean-filed approximation. So in the BEC limit we must be restricted in the following discussion to the temperatures much lower than the temperature of superconductive transition: $0 \leq T << T_{\text{Bose}}$, where $T_{\text{Bose}} = [n/2\zeta(3/2)]^{2/3}\pi/m$ [see e.g. [2,4]].

A special care should be taken when a mean-field approximation is used for the description of a two-dimensional system. It is well-known, that a straightforward calculations of the next-to-leading order corrections gives that the gap should be exactly zero at any finite temperature in 2+1 dimensions. This is due to the fact that, according to standard dimensional reduction arguments, a 2+1-dimensional system is effectively two dimensional at high temperature and in two dimensions there is no Goldstone boson as it is articulated in Coleman-Mermin-Wagner-Hohenberg theorem [23]. However as it was shown by Witten [27] (see also [21,24,22]) a direct calculation of corrections misses essential physics of a
two-dimensional problem and a mean-field results still have sense under certain conditions in 2D. The situation is following: the fluctuations can be made arbitrarily weak by decreasing temperature in 2+1 dimensions (or e.g. increasing N in 2D zero temperature calculations in [27,21,24]) and then employing a “modulus-phase variables” \( \Delta = |\Delta|e^{i\theta} \) one can observe that the system possesses a very well-defined “mexican hat” effective potential that determines the gap modulus. Due to phase fluctuations in the degenerate valley of the potential, the average of the complex gap function is zero, however there exist a gap locally (i.e. in some sense the system in its low energy domain degenerates to a nonlinear sigma model). In 2+1 dimensions, as the temperature approaches zero the thermal fluctuations in the degenerate valley of the effective potential gradually vanish and at \( T = 0 \) a local gap becomes a real gap. Existence of the local gap modulus \( \Delta \) does not contradict the Coleman-Mermin-Wagner-Hohenberg theorem since \( \Delta \) is neutral under \( U(1) \) transformations. Thus at low temperature in 2+1 dimensions there appears an “almost” Goldstone boson that becomes a real Goldstone boson at exactly zero temperature. At low temperatures we can neglect contribution from weak phase fluctuation at temperatures much lower than the temperature of the Kosterlitz-Thouless transition, which in the weak coupling limit approximately coincides with the temperature of pair formation and in strong-coupling limit reaches a plateau value: \( T_{KT} = \frac{\epsilon_F}{8} = \frac{\pi n}{8m} \), where \( \epsilon_F = (\pi/m)n \) is the Fermi energy of free fermions with the carrier density \( n \) and mass \( m \) [15,18,14,6].

Let us now outline how finite temperature quantities will be derived. We start with inspection of the gap \( \Delta \) behavior at low temperature. \( \Delta(T) \) can be expressed with the help of the analytic zero-temperature results from [9]. For example in three dimension we can write an equation that relates the gap at zero temperature with the gap at finite temperature at a fixed crossover parameter \( x_0 \) (which enters implicitly \( \Delta(0) \)):

\[
\int_{-\mu}^{\infty} d\xi \frac{\sqrt{\xi + \mu}}{\sqrt{\xi^2 + \Delta(0)^2}} = \int_{-\mu}^{\infty} d\xi \frac{\sqrt{\xi + \mu}}{\sqrt{\xi^2 + \Delta(T)^2}} \tanh \frac{\sqrt{\xi^2 + \Delta(T)^2}}{2T}.
\]  

This equation should be solved self-consistently with eq. (3). We must observe that the above system of equations, in contrast to zero-temperature calculations has the temperature as an extra parameter. Thus we need to specify in what model we are studying temperature effects with two most general options being: (i) “fixed chemical potential model” - i.e. when we do not fix the carrier density but assume the presence of a reservoir which provides us with a temperature-independent chemical potential \( \mu = \mu(1/k_F a_s; T = 0) \) or (ii) “fixed carrier” density model - i.e. when \( n \) is fixed and \( \mu \) varies with temperature. We choose the first option since such a fixed-\( \mu \) model is the most convenient for deriving asymptotic results for the finite-temperature behavior of the system. However the choice of the model is not principal since from (3) it is seen that in a “fixed density” regime the chemical potential in BCS and BEC limits depends very weakly on temperature in comparison with the dependence on the coupling strength in the regimes where our formulas are valid. Moreover the temperature dependence of the chemical potential in the entire crossover region was calculated numerically in 2D in [14] and it is small comparing to its variation with coupling strength in the temperature range \( 0 < T < T_{KT} \). So the results are similar in both cases of the presence of a particle reservoir that provides temperature independent chemical potential when carrier density varies or in the model of temperature independent carrier density.

In our calculation we use \( x_0 \) as the most convenient crossover parameter, since it depends via the simple relation \( x_0 = \mu/\Delta \) on the chemical potential which can be measured rather directly experimentally [28]. The parameter \( x_0 \) ranges from \( -\infty \) in the strong-coupling (Bose-Einstein) limit to \( \infty \) in the weak-coupling (BCS) limit. The relation between \( x_0 \) and the inverse reduced coupling strength between the electrons \( 1/k_F a_s \) is plotted for three-dimensional system in Fig. 3. The corresponding relation (16) in two dimensions between \( x_0 \) and the bound state energy \( \epsilon_0 \) of the electron pairs is plotted on Fig. 4.
FIG. 3. Dependence of $1/k_F a_s$ on the crossover parameter $x_0$ in three dimensions at zero temperature.

FIG. 4. Dependence of $\epsilon_0/\epsilon_F$ on the crossover parameter $x_0$ at zero temperature.
B. The gap functions

Let us now turn to the region near zero temperature, where the mean-field approximation gives an exact result for the gap function. From (17) we extract the asymptotic behavior in the three-dimensional case at low $T$ having $T/\Delta(0)$ as a small parameter. For this purpose let us first rewrite (17) in three dimensions as:

$$
\int_{-\mu}^{\infty} d\xi \left[ \frac{\sqrt{\xi + \mu}}{\sqrt{\xi^2 + \Delta(0)^2}^2} - \frac{\sqrt{\xi + \mu}}{\sqrt{\xi^2 + \Delta(T)^2}^2} \right] = - \int_{-\mu}^{\infty} d\xi \frac{\sqrt{\xi + \mu}}{\sqrt{\xi^2 + \Delta(T)^2}^2} \left[ 1 - \tanh \frac{\sqrt{\xi^2 + \Delta(T)^2}}{2T} \right].
$$

In the region $x_0 > 1$ one can assume density of states to be roughly constant, since the integrand of (18) is peaked in the narrow region near $\xi = 0$. Then the integral in the r.h.s of (18) can be written as

$$
2\sqrt{\pi} \int_{-\mu}^{\infty} d\xi \frac{1}{\sqrt{\xi^2 + \Delta(T)^2}^2} \exp \left[ -\frac{\sqrt{\xi^2 + \Delta(T)^2}}{T} \right].
$$

This integral can be calculated e.g. by changing the integration variable to $y = \sqrt{\xi/\Delta(0)}^2 + 1 = 1$ and expanding the factor before exponent. The result is expressed via the error function and we arrive at the following expression for the behavior of the gap function near $T = 0$ in the region $x_0 > 1$

$$
\Delta(T) = \Delta(0) - \Delta(0) \sqrt{\frac{\pi}{2}} \frac{T}{\Delta(0)} \exp \left[ -\frac{\Delta(0)}{T} \right] \left[ 1 + \text{erf} \left( \sqrt{\frac{x_0^2 + 1 - 1}{T/\Delta(0)}} \right) \right],
$$

where erf($x$) is the error function. Since the density of states is nearly constant in this limit, the same equation holds in two-dimensions—apart from a modified gap $\Delta(0)$ given by (14).

In the weak-coupling limit, $x_0 = \mu/\Delta(0)$ tends to infinity, and the expression above approaches exponentially fast the well-known BCS result:

$$
\Delta(T) = \Delta(0) - \left[ 2\pi \Delta(0) T \right]^{1/2} \exp \left[ -\frac{\Delta(0)}{T} \right]
$$

For strong couplings with $x_0 < -1$ the integration range, in contrast to the above case, does not include the point $\xi = 0$, so we write the r.h.s of (18) as:

$$
2\sqrt{\Delta(0)} \int_{-\infty}^{x_0} \frac{\sqrt{\xi/\Delta(0) + x_0}}{\sqrt{\xi/\Delta(0) + x_0}^2 + \Delta(T)/\Delta(0)^2} \exp \left[ -\frac{\sqrt{\xi/\Delta(0)^2 + \Delta(T)/\Delta(0)^2}}{T/\Delta(0)} \right] d\left( \frac{\xi}{\Delta(0)} \right)
$$

This integral can be calculated e.g. by changing the integration variable to $v = \sqrt{(\xi/\Delta(0))^2 + 1} - \sqrt{x_0^2 + 1}$ and expanding the factor before exponent so that the above integral is reduced to:

$$
2\sqrt{\Delta(0)} \frac{x_0}{|x_0|} \exp \left[ -\frac{x_0^2 + 1}{T/\Delta(0)} \right] \int_{0}^{\infty} \exp \left[ -\frac{\Delta(0)}{T} v \right] \sqrt{v} dv
$$

Thus, we find the behavior of the gap function at $x_0 < -1$:

$$
\Delta(T) = \Delta(0) - \frac{8}{\sqrt{\pi}} \frac{x_0}{\sqrt{-x_0} \sqrt{\Delta(0)}} \exp \left[ -\frac{\mu^2 + \Delta^2(0)}{T} \right].
$$

From Eq. (24) we see that near $T = 0$ the gap $\Delta(T)$ tends in the strong-coupling limit exponentially to $\Delta(0)$, forming plateau near $T = 0$. 


In two dimensions we arrive at similar result: an exponentially growing plateau near $T = 0$ in the strong coupling limit:

$$\Delta(T) = \Delta(0) - \frac{\Delta(0)}{2} E_1\left(\frac{\sqrt{\Delta(0)^2 + \mu^2}}{T}\right),$$

(25)

where $E_1$ is the exponential integral $E_1(z) = \int_1^{\infty} e^{-t} dt$. The plateau formation in the low temperature solution for the gap function in a strong-coupling regime (see Fig. 5) is an indication of the suppression of a pairbreaking effects in low temperature domain. One can however observe that in contrast to BCS regime in the BEC regime the suppression comes from a large negative chemical potential in the exponent $|\mu| >> |\Delta|$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.png}
\caption{“Plateau” formation of the gap function at low temperature in three dimensions. In the BCS limit the thermal fluctuations start breaking fermion pairs already at low temperatures which results in the absence of plateau of $\Delta(T)/\Delta(0)$. In the BEC limit in contrast we have a plateau near zero temperature. Inclusion of Gaussian corrections in the BEC limit leads to depletion of the average order parameter due to depletion of macroscopic occupation of zero momentum level. The order parameter in this limit becomes zero at $T_c = \left[n/2\zeta(3/2)\right]^{2/3} \pi/m \approx 0.218 \epsilon_F$. This region is not plotted on the above figure.}
\end{figure}

C. The thermodynamics

Let us now calculate thermodynamical quantities near $T = 0$. For the thermodynamic Gibbs potential $\Omega(T, \mu, V)$ we have

$$\Omega = \sum_k \left\{ \frac{\Delta^2}{2\sqrt{\xi_k^2 + \Delta^2}} \tanh \frac{\sqrt{\xi_k^2 + \Delta^2}}{2T} - 2T \log \left[ 2 \cosh \frac{\sqrt{\xi_k^2 + \Delta^2}}{2T} \right] + \xi_k \right\}.$$  

(26)

Here and in the sequel in this section, $\Delta(0)$ will be replaced by $\Delta$. In three dimensions, Eq. (26) turns into the
\[
\frac{\Omega}{V} = \kappa_3 \int_{-\mu}^{\infty} d\xi \sqrt{\xi + \mu} \left[ \frac{\Delta^2}{2\sqrt{\xi^2 + \Delta^2}} \tanh \frac{\sqrt{\xi^2 + \Delta^2}}{2T} - 2T \log \left( 2 \cosh \frac{\sqrt{\xi^2 + \Delta^2}}{2T} \right) + \xi \right],
\]
(27)

In two dimensions, we obtain instead:
\[
\frac{\Omega}{V} = \kappa_2 \int_{-\mu}^{\infty} d\xi \left[ \frac{\Delta^2}{2\sqrt{\xi^2 + \Delta^2}} \tanh \frac{\sqrt{\xi^2 + \Delta^2}}{2T} - 2T \log \left( 2 \cosh \frac{\sqrt{\xi^2 + \Delta^2}}{2T} \right) + \xi \right],
\]
(28)

We regularize the thermodynamic potential \( \Omega_s \) of the condensate subtracting \( \Omega_n = \Omega(\Delta = 0) \). At \( T = 0 \) and for weak couplings this is found to depend on \( \mu \) and \( \Delta \) as follows:
\[
\frac{\Omega_s}{V} \equiv \frac{\Omega - \Omega_n}{V} = \kappa_3 \sqrt{\mu} \left[ -\Delta^2 + \frac{1}{2} \mu |\mu| - \frac{1}{2} \mu \sqrt{\mu^2 + \Delta^2} \right]
\]
(29)

In the BCS limit \( (x_0 \to \infty) \) this reduces to the well-known result
\[
\frac{\Omega_s}{V} = \kappa_3 \sqrt{\mu} \left[ -\frac{\Delta^2}{2} \right].
\]
(30)

In two dimensions, we have a formula valid for any strength of coupling or carrier density:
\[
\frac{\Omega_s}{V} = \kappa_2 \left[ -\frac{\Delta^2}{4} + \frac{1}{2} \mu |\mu| - \frac{1}{2} \mu \sqrt{\mu^2 + \Delta^2} \right],
\]
(31)

In the opposite limit of strong couplings, we find in three dimensions:
\[
\frac{\Omega}{V} = -\frac{\pi}{64} \kappa_3 \Delta^{5/2} (x_0)^{-3/2}.
\]
(32)

The gap \( \Delta(0) \) has by Eq. (11) the strong-coupling limit \( \Delta(0) \approx \epsilon_F [16/3\pi]^{3/2} |x_0|^{1/3} \) yielding the large-\( x_0 \) behavior
\[
\frac{\Omega}{V} \sim -\kappa_3 \epsilon_F^{5/2} \frac{\pi}{64} \left( \frac{16}{3\pi} \right)^{15/4} |x_0|^{-2/3}.
\]
(33)

In two dimensions, we substitute the gap function \( \Delta \) of Eq. (14), into the thermodynamic potential (28), and obtain for strong couplings an interesting result:
\[
\frac{\Omega}{V} \equiv 0
\]
(34)

Let us now turn to the entropy. In three dimensions near \( T = 0 \) it is given for weak couplings by:
\[
\frac{S}{V} = \kappa_3 \sqrt{\mu} \left\{ \sqrt{\frac{2\pi\Delta^3}{T}} \exp \left( -\frac{\Delta}{T} \right) \left[ 1 + \text{erf} \left( \sqrt{\frac{\sqrt{x_0^2 + 1} - 1}{T/\Delta}} \right) \right] + 2\mu \exp \left( -\sqrt{\frac{\mu^2 + \Delta^2}{T}} \right) \right\},
\]
(35)

For \( \mu/\Delta \to \infty \), this reduces correctly to the BCS result:
\[
\frac{S}{V} = \kappa_3 \sqrt{\mu} \sqrt{\frac{8\pi\Delta^3}{T}} \exp \left( -\frac{\Delta}{T} \right)
\]
(36)

In two dimensions, the result is similar apart from the fact that \( \Delta = \Delta(0) \) should be given by Eq. (14) and \( \kappa_3 \sqrt{\mu} \) should be replaced by \( \kappa_2 \). In the strong-coupling limit where \( \mu/\Delta \ll -1 \), we have for the entropy in three dimensions
\[
\frac{S}{V} = \kappa_3 \frac{\sqrt{\pi}}{4} T^{1/2} \sqrt{\mu^2 + \Delta^2} \exp \left( -\frac{\sqrt{\mu^2 + \Delta^2}}{T} \right),
\]  
and in two dimensions:
\[
\frac{S}{V} = -2\kappa_2 \mu \exp \left( \frac{\sqrt{\mu^2 + \Delta^2}}{T} \right) \tag{38}
\]

From the entropy, we easily derive the heat capacity at a constant volume \(c_V\). In three dimensions it is given near \(T = 0\) for weak and moderate couplings by
\[
c_V = \kappa_3 \sqrt{\mu} \sqrt{2\pi \Delta^3} \left\{ \frac{\Delta}{T^{3/2}} \exp \left( -\frac{\Delta}{T} \right) \left[ 1 + \text{erf} \left( \frac{\sqrt{x_0^2 + 1} - 1}{T/\Delta} \right) \right] \right\} \tag{39}
\]
reducing in the limit \(x_0 \to \infty\) to the BCS result
\[
c_V = \kappa_3 \sqrt{\mu} \sqrt{2\pi \Delta^3} \frac{2\Delta}{T^{3/2}} \exp \left( -\frac{\Delta}{T} \right). \tag{40}
\]

In two dimensions, the weak-coupling behavior is the same with the factor \(\kappa_3 \sqrt{\mu}\) replaced by \(\kappa_2\) while the strong-coupling behavior in three dimensions is
\[
c_V = \kappa_3 \frac{\sqrt{\pi}}{4} T^{-1/2} (\mu^2 + \Delta^2) \exp \left( -\frac{\sqrt{\mu^2 + \Delta^2}}{T} \right) \tag{41}
\]
and in two dimensions
\[
c_V = 2\kappa_2 \frac{\mu^2}{T} \exp \left( -\frac{\sqrt{\mu^2 + \Delta^2}}{T} \right). \tag{42}
\]

IV. CONCLUSION

The BCS-BEC crossover and related phenomena is now a subject of increasing interest in many branches of physics. In this paper we have presented simple asymptotical results for one of the important aspects of this phenomenon in superconductors. Namely we studied the behavior of thermodynamic functions when a system crosses over from the BCS superconductivity to the Bose condensate of tightly bound pairs. The first observation that could be made analyzing the thermodynamic expressions is that the crossover takes place in a quite a narrow region \(1 > x_0 > -1\) which is in agreement with previous studies.

While the crossover is known to be continuous, the thermodynamic functions assume an exotic form in the regime of strong attraction or low carrier density. The interesting feature is that a modified gap function \(\sqrt{\Delta^2 + \mu^2}\) enters all the expressions in the BEC limit in a similar way as the gap function \(\Delta\) enters thermodynamic expressions in the BCS limit. Since in the BEC regime \(\Delta \ll -\mu\), the chemical potential is in some sense playing the same role as the gap function in the BCS theory. This result, that may seem surprising from the point of view of the BCS theory, has the following roots: The gap in the spectrum of single-particle excitations has a special feature \([3],[4],[5]\) when the chemical potential changes its sign. The sign change occurs at the minimum of the Bogoliubov quasiparticle energy \(E_k\) where this energy defines the gap energy in the quasiparticle spectrum:
\[
E_{\text{gap}} = \min \left( \xi_k^2 + \Delta^2 \right)^{1/2}. \tag{43}
\]
Thus, for positive chemical potential, the gap energy is given directly by the gap function \( \Delta \), whereas for negative chemical potential, it is larger than that:

\[
E_{\text{gap}} = \begin{cases} 
\Delta & \text{for } \mu > 0, \\
(\mu^2 + \Delta^2)^{1/2} & \text{for } \mu < 0.
\end{cases}
\]

That means that for the positive values of the chemical potential the gap function has the same meaning as the standard superconductive gap. In contrast, in the Bose limit, when chemical potential goes below the bottom of the band, one should distinguish between the two notions of the “gap”. At first, there is the order parameter \( \Delta \) that reaches zero at \( T_c \) [see e.g. [5]]. Also, in this limit, there exist the modified gap function (44) that tends to \( |\mu| = E_b/2 \), where \( E_b = 1/ma^2 \) thus being proportional to the binding energy of the pairs. So when one is concerned about e.g. low-temperature thermodynamic functions one should understand under the “gap” basically the chemical potential rather than the order parameter \( \Delta \).

Other well-known and to some extend similar features arising when a system crosses over from BCS to BEC limit are: (i) the appearance of two characteristic temperatures of different physical origin \( T_c \) and \( T^* \) in BEC limit [4,2] in contrast to only one characteristic temperature \( T_c \) in the BCS limit; (ii) the separation of notions of the Cooper pair size and coherence length in strong coupling condensate which in contrast coincide in the BCS limit.

The above results for thermodynamical quantities once again illustrate the interesting circumstance of the essentially richer nature of a strong coupling condensate comparing to a BCS condensate that helps to understand better the phenomenon of symmetry breakdown in Fermi systems.

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APPENDIX A: THERMODYNAMICS NEAR CRITICAL TEMPERATURE OF SUPERCONDUCTORS WITH MODERATELY STRONG COUPLING STRENGTH

In this Appendix we present expressions for the behavior of the gap and the thermodynamic functions near \( T_c \) in superconductors with moderately strong coupling strength. We employ a mean-field approximation and thus our expressions are not valid in the crossover region where one should incorporate fluctuation corrections in the regime near \( T_c \).

In the regime of weak or moderately strong attraction and also for moderately low carrier density the gap function behaves near \( T_c \) as follows:

\[
\left[ \frac{\Delta(T)}{2T_c} \right]^2 = \frac{1}{4} \left[ \frac{1}{\mu/2T_c} - \frac{\mu/2T_c}{(\mu/2T_c)^2 + \tanh \frac{\mu}{2T_c}} \right]^2 + \left( \frac{2}{\pi} \right)^2 \left( 1 + \frac{2}{\pi} \arctan \frac{\mu}{\pi T_c} \right).
\]

In the limit \( \mu/2T_c \to \infty \) this tends to the BCS result

\[
\frac{\Delta(T)}{T_c} \simeq 3 \sqrt{1 - \frac{T}{T_c}}.
\]

The ratio of zero temperature gap to the critical temperature has the following dependence on crossover parameter close to the BCS regime:
\[ \frac{\Delta(0)}{T_c} = \frac{\pi}{e^\gamma} \left( 1 - \frac{\Delta(0)^2}{4\mu^2} \right)^{-1/2} = \frac{\pi}{e^\gamma} \left( 1 - \frac{1}{4x_0^2} \right)^{-1/2} \]  

(A.3)

Whereas the critical temperature has the following dependence on \( x_0 \):

\[ \frac{T_c}{e_F} \approx \frac{e^\gamma}{\pi} \left( \frac{1}{x_0} - \frac{3}{8x_0^3} \right) \]  

(A.4)

The thermodynamic potential in three dimensions in the weak-coupling regime near \( T_c \) is given by

\[ \frac{\Omega_s}{V} = -\kappa_3 \sqrt{\mu} \left\{ \frac{(T_c - T)\Delta^2}{2T_c} \left[ 1 + \tanh \frac{\mu}{2T_c} \right] + \frac{\Delta^4}{4(2T_c)^2} \left[ \frac{1}{4} \left( \frac{1}{\mu/2T_c} - \frac{1}{(\mu/2T_c)^2} \tanh \frac{\mu}{2T_c} \right) + \left( \frac{2}{\pi} \right)^2 \left( 1 + \frac{2}{\pi} \arctan \frac{\mu}{\pi T_c} \right) \right] \right\}. \]  

(A.5)

In the BCS limit, this reduces to the well-known formula:

\[ \frac{\Omega_s}{V} = -\kappa_3 \sqrt{\mu} \Delta^2 \left( 1 - \frac{T}{T_c} - \frac{1}{2\pi^2} \frac{\Delta^2}{T_c^2} \right) \]  

(A.6)

The entropy behaves near \( T_c \) in three dimensions in the weak-coupling regime like

\[ \frac{S_s}{V} = \frac{S - S_n}{V} = -\kappa_3 \sqrt{\mu} \frac{\Delta^2}{2T_c} \left[ 1 + \tanh \left( \frac{\mu}{2T_c} \right) \right] \]  

(A.7)

with the BCS limit

\[ \frac{S_s}{V} = -\kappa_3 \sqrt{\mu} \frac{\Delta^2}{T_c}. \]  

(A.8)

In order to derive the specific heat we must take into account the temperature dependence of the gap.

In three dimensions, we find in the weak-coupling region near \( T_c \):

\[ \frac{C_s}{V} = 2T\kappa_3 \sqrt{\mu} \frac{\left( 1 + \tanh \frac{\mu}{2T_c} \right)^2}{\frac{1}{4} \left[ \frac{1}{\mu/2T_c} - \frac{1}{(\mu/2T_c)^2} \tanh \frac{\mu}{2T_c} \right] + \left( \frac{2}{\pi} \right)^2 \left( 1 + \frac{2}{\pi} \arctan \frac{\mu}{\pi T_c} \right)}, \]  

(A.9)

which has the well-known BCS limit:

\[ \frac{C_s}{V} \approx \kappa_3 \sqrt{\mu} \pi^2 T_c. \]  

(A.10)

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