Quasi-particles, thermodynamic consistency and the gap equation

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Abstract

The thermodynamic properties of superconducting electrons are usually studied by means of the quasi-particles distribution; but in this approach, the ground state energy and the dependence of the chemical potential on the electron density cannot be determined. In order to solve these problems, the thermodynamic potentials are derived by means of the Bogoliubov-Valatin formalism. The thermodynamic potentials can be obtained by computing the free energy of a gas of quasi-particles, whose energy spectrum is conditional on the gap function. However, the nontrivial dependence of the gap on the temperature jeopardises the validity of the standard thermodynamic relations. In this article it is shown how the thermodynamic consistency (*i.e.* the validity of the Maxwell relations) is recovered, and the correction terms to the quasi-particles potentials are computed. It is shown that the Bogoliubov-Valatin transformation avoids the problem of the thermodynamic consistency of the quasi-particle approach; in facts, the correct identification of the variables, which are associated with the quasi-particles, leads to a precise calculation of the quasi-particles vacuum energy and of the dependence of the chemical potential on the electron density. The stationarity condition for the grand potential coincides with the gap equation, which guarantees the thermodynamic consistency. The expressions of various thermodynamic potentials, as functions of the (T, V, N) variables, are produced in the low temperature limit; as a final check, a rederivation of the condensation energy is presented.

1   Introduction

The Bogoliubov transformation is one of the main discoveries in mathematical physics. In this article it is shown how to compute the thermodynamic potentials —functions of the (T, V, N) variables— in superconductivity by means of the Bogoliubov transformation. It is demonstrated

that the Bogoliubov transformation avoids the problem of the thermodynamic consistency of the quasi-particle approach. The quasi-particles vacuum energy and the dependence of the chemical potential on the electron density are derived.

In the low temperature limit, the thermodynamic behaviour of any macroscopic physical system is determined by the structure of the energy levels of the system which belong to a neighbourhood of the ground state energy. The experimental data show that, usually, these energy levels are organized in such a way that one can give a quite good description of their thermodynamic properties by means of a gas of quasi-particles [1, 2]. The energy spectrum of a single quasi-particle is specified by its dispersion relation, which is determined by the nature of the interactions among the "atoms" or the "elementary constituents" of the system.

Let us consider the framework in which the gas of quasi-particles describes the thermal fluctuations of the system above its ground state. In this formalism, the number of quasi-particles is not conserved —in facts it vanishes at zero temperature— and therefore the quasi-particles chemical potential is zero. Even if the system is composed of strongly interacting atoms —like in a quantum liquid— the quasi-particles are weakly interacting, and then one can determine, with a good approximation, the thermodynamic potentials of the system. Indeed, in the low temperature limit the density of quasi-particles becomes very low, so that their mutual interactions produce minor effects. Thus a crucial part of the information on the thermal properties of the whole system is mainly contained in the form of the dispersion relation of a single quasi-particle. Let $\varepsilon(\boldsymbol{p})$ be the energy of a single quasi-particle in the state labelled by the value $\boldsymbol{p}$ of the momentum. The function $\varepsilon(\boldsymbol{p})$ can be a rather complicated function of the momentum, which can be determined by the experimental data, or it can be deduced —in some approximated form— from the hamiltonian of the system. In superconductors, for instance, the dispersion relation for a single quasi-particle [3, 4] assumes the form

$$\varepsilon(\boldsymbol{p}) \simeq \left[\left(\boldsymbol{p}^2/2m - \mu \right)^2 + \Delta_{\boldsymbol{p}}^2 \right]^{1/2} , \tag{1.1}$$

where μ denotes the chemical potential for the electrons. The gap function $\Delta_{\boldsymbol{p}}$ can be different from zero in a neighbourhood of the surface of the Fermi sphere and satisfies

$$\Delta_{\boldsymbol{p}} = \begin{cases} \Delta(T) & \text{when } |\boldsymbol{p}^2/2m - \mu| \leq \delta E \simeq \hbar\omega_D ; \\ \\ 0 & \text{otherwise;} \end{cases} \tag{1.2}$$

in which ω_D indicates the Debye frequency of the ions lattice. The gap $\Delta(T)$ is not vanishing when the temperature T takes values below the critical value T_c, and $\Delta(T) = 0$ for $T \geq T_c$. As a result, the energy ε of a single quasi-particle nontrivially depends on the temperature, $\varepsilon = \varepsilon(\boldsymbol{p}, T)$. But when the dispersion relation $\varepsilon(\boldsymbol{p}, T)$ nontrivially depends on the temperature, the standard expressions of the thermodynamic potentials —derived in statistical mechanics— for a gas of weakly interacting constituents do not satisfy the thermodynamic relations (or Maxwell relations).

More precisely, if A represents a standard thermodynamic potential which is computed in statistical mechanics when the atomic energy $\varepsilon_0(\boldsymbol{p})$ does not depend on the temperature, let us denote by A_q the corresponding potential for the gas of quasi-particles which is obtained from A by means of the substitution $\varepsilon_0(\boldsymbol{p}) \to \varepsilon(\boldsymbol{p}, T)$. For instance, the free energy F_q and the

internal energy U_q of a gas of noninteracting quasi-particles with energy $\varepsilon(\boldsymbol{p}, T)$, satisfying the Fermi-Dirac statistics, are given by

$$F_q(T, V) = -\frac{kTVg}{h^3} \int d^3p \, \ln\left(1 + e^{-\varepsilon(\boldsymbol{p},T)/kT}\right) \; , \qquad (1.3)$$

and

$$U_q(T, V) = \frac{Vg}{h^3} \int d^3p \, \frac{\varepsilon(\boldsymbol{p}, T)}{e^{\varepsilon(\boldsymbol{p},T)/kT} + 1} \; , \qquad (1.4)$$

where g denotes the spin degeneration factor. When the thermodynamic relations are satisfied, the entropy S is given by $S = -\partial F(T, V)/\partial T$; and since $F = U - TS$, one has $U = F - T(\partial F/\partial T)$. However, if $[\partial \varepsilon(\boldsymbol{p}, T)/\partial T] \neq 0$, one finds

$$U_q \neq F_q - T\left(\frac{\partial F_q}{\partial T}\right)_V \; , \qquad (1.5)$$

and therefore expressions (1.3) and (1.4) do not satisfy the thermodynamic relations.

In addition to their agreement with experiments, the thermodynamic relations codify to some extent the laws of thermodynamics and are necessary for the sake of logic. The requirement of validity of the thermodynamic relations will be called the thermodynamic consistency. The thermodynamic consistency implies that, in general, the thermodynamic potentials of the macroscopic systems cannot be exactly equal to the potentials A_q of the quasi-particles. The presence of adjusting terms δA_q is needed in order to rectify the A_q expressions and make the final combinations $A_q + \delta A_q$ correct. As far as the computation of δA_q is concerned, the knowledge of the quasi-particles distribution is of no help, because δA_q is essentially determined by the quasi-particles vacuum energy.

One of the purposes of the present article is to produce the correction terms to the quasi-particles potentials in the case of superconductivity by means of the Bololiubov-Valatin formalism. It is shown that the accurate determination of the quasi-particles vacuum energy completes the construction of the thermodynamic potentials satisfying the Maxwell relations. It is verified that, in agreement with the Landau principle, the value of the gap corresponds to a stationary point of the grand potential $\Omega(T, V, \mu)$. Then the expressions of the thermodynamically consistent potentials as functions of the (T, V, N) variables are obtained, and how the chemical potential is related with the electron density is determined. As a final check, a derivation of the superconducting condensation energy from $\Omega(T, V, \mu)$ is presented.

The thermodynamic consistency in the presence of nontrivial medium-dependent dispersion relation has been considered for instance by Shanenko, Yujalova and Yukalov [5, 6] in the case of clustering matter, and by Gorenstein and Yang [7] in the case of a gluon plasma. This issue has been elaborated also in [8, 9, 10, 11, 12]. The Landau principle, which can be interpreted as an equilibrium condition for ordinary thermal states, implies the thermodynamic consistency. It as been argued [12] that, conversely, the validity of the thermodynamic consistency does not necessarily imply the Landau principle. The results for the superconducting electrons are in agreement with the analysis of Ref.[7].

In superconductivity, the dependence of the thermodynamic potentials on the statistical mean value N of the number of electrons is a rather nontrivial issue because, when $T < T_c$, the $U(1)$ symmetry which is related to the number of electrons in superconductors is broken [3, 4]. The solution to this problem which is presented in the following chapters and the outcomes

of the computed thermodynamic potential $\Omega(T, V, \mu)$ are in agreement with the known results [3, 4, 13, 14] on superconductivity. In the present work it is shown that the identification of the variables which are associated with the quasi-particles leads to a precise determination of the quasi-particles vacuum energy. The method, which is presented here to solve this question, can find applications also in the study of topological superconductivity and in the new developments on the topological states of matter [15, 16, 17, 18, 19, 20, 21, 22, 23, 24].

The basic concepts which are connected with the use of the quasi-particles distribution are briefly recalled in Section 2. Starting from the BCS hamiltonian, in Section 3 the Bogoliubov-Valatin formalism [25, 26] is used to determine the grand potential Ω, according to the procedure envisaged for instance by Rickayzen [27]. By means of a Bogoliubov transformation acting on the creation and annihilation operators of the electron fluctuations around the Fermi sphere, the full expression of $\Omega(T, V, \mu)$ satisfying the Maxwell relations is obtained. The thermodynamic consistency of the result is discussed in Section 4, where a new derivation of the gap equation is described. In Section 5 the relation connecting the chemical potential with the electron density is derived, and the consistent expressions of various thermodynamic potentials —functions of the (T, V, N) variables— of the superconduting electrons are produced in the low temperature limit.

2   Quasi-particles distribution

Let us briefly recall the basic notions which are related to the use of the quasi-particles formalism. The description of the low temperature physics by means of quasi-particles represents a phenomenological approach in which the dispersion relation of a single quasi-particle non-trivially depends on the macroscopic variables of the material $\varepsilon(\boldsymbol{p}) = \varepsilon(\boldsymbol{p}, T, \mu, ...)$. Thus, in addition to the temperature, the failure of the thermodynamic consistency for the quasi-particle potentials A_q really concerns several state variables. In certain circumstances the dependence of ε on these variables is weak enough so that, in a limited range of variability, one can assume [28] that ε only depends on the momentum. But in general —and in particular when a phase transition occurs— one cannot neglect the dependence of ε on the macroscopic variables; this dependence will be denoted by $\varepsilon = \varepsilon(\boldsymbol{p}, T)$.

As it has been suggested by Landau [2], a possible way to connect the thermodynamic potentials of the system with the quasi-particles functions makes use of the quasi-particles distribution. The only thermodynamic potential whose absolute value is fixed —and cannot be modified by any additive constant— is the entropy S,

$$S = k \, \ln\big\{ \text{number of microstates with fixed macro conditions} \big\} \, . \tag{2.1}$$

Since the quantum states of the system are described (in the low temperature limit) precisely by the gas of quasi-particles, the entropy of the system is equal to the entropy of the quasi-particles gas. For noninteracting quasi-particles, the number of microstates in a given macrostate can be determined by means of the distribution $n_{\boldsymbol{p}}$ of the quasi-particles. Indeed, in the quantum case of Fermi statistics, the analogue of the Boltzmann H-functional is given [2] by

$$S = -\frac{V g k}{h^3} \int d^3 p \, [n_{\boldsymbol{p}} \ln n_{\boldsymbol{p}} + (1 - n_{\boldsymbol{p}}) \ln(1 - n_{\boldsymbol{p}})] \, . \tag{2.2}$$

4

Let us recall that, in the case of particles with vanishing chemical potential, the entropy represents the thermodynamic potential for the variables (U, V). This means that, with fixed (U, V), the stable thermal state of the system corresponds to a maximum of S. Therefore the distribution $n_{\boldsymbol{p}}$ can be determined by the requirement that, for fixed (U, V), the variation of S with respect to a generic fluctuation $\delta n_{\boldsymbol{p}}$ must vanish. The associated (conditioned) variational principle takes the form

$$\frac{\delta S}{\delta n_{\boldsymbol{p}}} - \lambda \frac{\delta U}{\delta n_{\boldsymbol{p}}} = 0 \; , \tag{2.3}$$

where the value of the Lagrange multiplier λ is given by $\lambda = 1/T$ as a consequence of the Maxwell relation $T dS - dU - P dV = 0$. Because of the explicit dependence (2.2) of S on V, there is no need to introduce a Lagrange multiplier for the volume. Since a modification of $n_{\boldsymbol{p}}$ causes the following change in the energy

$$\delta U = \frac{V g}{h^3} \int d^3 p \, \varepsilon(\boldsymbol{p}, T) \, \delta n_{\boldsymbol{p}} \; , \tag{2.4}$$

the solution of equation (2.3) is given precisely by the Fermi-Dirac distribution

$$n_{\boldsymbol{p}} = \frac{1}{e^{\varepsilon(\boldsymbol{p}, T)/kT} + 1} \; . \tag{2.5}$$

By using equation (2.5) several variables can be computed. Unfortunately, the knowledge of the distribution (2.5) —or of $S(T, V)$— alone is not enough to determine all the potentials; for instance, the complete expressions of the free energy F and of the internal energy U cannot be obtained from equation (2.5).

3 Computation of the grand potential

The low energy BCS hamiltonian [3] for conducting electrons in superconductor metals can be written as

$$H_{BCS} = \sum_{\boldsymbol{p},s} \frac{\boldsymbol{p}^2}{2m} b_{\boldsymbol{p},s}^\dagger b_{\boldsymbol{p},s} + \sum_{\boldsymbol{p},q} U_{\boldsymbol{p},\boldsymbol{q}} \, b_{\boldsymbol{p},+}^\dagger b_{-\boldsymbol{p},-}^\dagger b_{-\boldsymbol{q},-} b_{\boldsymbol{q},+} \; , \tag{3.1}$$

where $b_{\boldsymbol{p},s}^\dagger$ and $b_{\boldsymbol{p},s}$ denote the creation and annihilation operators for one electron in the state $|\boldsymbol{p}, s\rangle$, where $s = \pm$ refers to the value of one component of the spin,

$$
\begin{aligned}
\{b_{\boldsymbol{p},s} , b_{\boldsymbol{q},r}^\dagger\} &= \delta_{sr} \frac{h^3}{V} \delta(\boldsymbol{p} - \boldsymbol{q}) \quad , \\
\{b_{\boldsymbol{p},s} , b_{\boldsymbol{q},r}\} &= 0 = \{b_{\boldsymbol{p},s}^\dagger , b_{\boldsymbol{q},r}^\dagger\} \; .
\end{aligned}
\tag{3.2}
$$

The interaction kernel $U_{\boldsymbol{p},\boldsymbol{q}}$ is related to the amplitude of the electron-electron scattering. $U_{\boldsymbol{p},\boldsymbol{q}}$ does not depend on the values of the electron thermodynamic variables, as the temperature T, the volume V and the chemical potential μ. The main effects of the interactions between electrons in the superconducting materials —which are relevant for the superconducting phase transition— are found when $|\boldsymbol{p}^2/2m - \mu| \le \hbar \omega_D$ and $|\boldsymbol{q}^2/2m - \mu| \le \hbar \omega_D$, and in this region

$U_{\boldsymbol{p,q}}$ can be approximated by $-U_0/V$, where U_0 is a positive constant. The grand partition function $\mathcal{Q}$, which is defined by

$$\mathcal{Q}(T,V,\mu) = \text{Tr}\left[e^{-H_{BCS}/kT}e^{N\mu/kT}\right] \equiv \text{Tr}\left[e^{-H/kT}\right] \,, \tag{3.3}$$

can be interpreted as the partition function of a system with total hamiltonian

$$H = \sum_{\boldsymbol{p},s}\eta(p)\,b^{\dagger}_{\boldsymbol{p},s}b_{\boldsymbol{p},s} + \sum_{\boldsymbol{p},\boldsymbol{q}}U_{\boldsymbol{p},\boldsymbol{q}}\,b^{\dagger}_{\boldsymbol{p},+}b^{\dagger}_{-\boldsymbol{p},-}b_{-\boldsymbol{q},-}b_{\boldsymbol{q},+} \,, \tag{3.4}$$

in which the "effective" kinetic energy $\eta(p)$ of one electron (where $p = |\boldsymbol{p}|$) is given by

$$\eta(p) = \frac{\boldsymbol{p}^2}{2m} - \mu \,. \tag{3.5}$$

Since the trace (3.3) cannot be evaluated exactly, one can introduce a self-consistent approximation (some kind of a mean field approximation) which permits to proceed with the computation. In the grand canonical ensemble, let us introduce the statistical mean values

$$X_{\boldsymbol{p}} = \langle b_{-\boldsymbol{p},-}b_{\boldsymbol{p},+}\rangle \quad , \quad X_{\boldsymbol{p}}^* = \langle b^{\dagger}_{\boldsymbol{p},+}b^{\dagger}_{-\boldsymbol{p},-}\rangle \,. \tag{3.6}$$

In order to simplify the exposition, let us assume that $X_{\boldsymbol{p}}^* = X_{\boldsymbol{p}}$ (in facts, it turns out [3, 4, 13] that one can always choose the phases of the creation and annihilation operators in such a way that the mean values (3.6) are real). The couple of operators $b^{\dagger}_{\boldsymbol{p},+}b^{\dagger}_{-\boldsymbol{p},-}$ and $b_{-\boldsymbol{q},-}b_{\boldsymbol{q},+}$ can be written as the sum of their means values plus a fluctuation term,

$$\begin{aligned} b^{\dagger}_{\boldsymbol{p},+}b^{\dagger}_{-\boldsymbol{p},-} &= X_{\boldsymbol{p}} + (b^{\dagger}_{\boldsymbol{p},+}b^{\dagger}_{-\boldsymbol{p},-} - X_{\boldsymbol{p}}) \,, \\ b_{-\boldsymbol{q},-}b_{\boldsymbol{q},+} &= X_{\boldsymbol{q}} + (b_{-\boldsymbol{q},-}b_{\boldsymbol{q},+} - X_{\boldsymbol{q}}) \,. \end{aligned} \tag{3.7}$$

Now one can assume [13, 27] that the effects of the fluctuations are sufficiently small so that, inserting the identities (3.7) into the expression (3.4), the resulting term which is quadratic in the fluctuations can be neglected. One then finds

$$H \simeq \sum_{\boldsymbol{p},s}\eta(p)\,b^{\dagger}_{\boldsymbol{p},s}b_{\boldsymbol{p},s} - \sum_{\boldsymbol{p}}\Delta_{\boldsymbol{p}}X_{\boldsymbol{p}} + \sum_{\boldsymbol{p}}\left[\Delta_{\boldsymbol{p}}\,b^{\dagger}_{\boldsymbol{p},+}b^{\dagger}_{-\boldsymbol{p},-} + \Delta_{\boldsymbol{p}}\,b_{-\boldsymbol{p},-}b_{\boldsymbol{p},+}\right] \,, \tag{3.8}$$

where

$$\Delta_{\boldsymbol{p}} = \sum_{\boldsymbol{q}}U_{\boldsymbol{p},\boldsymbol{q}}X_{\boldsymbol{q}} \,. \tag{3.9}$$

In order to recover the quasi-particles description of the low temperature behaviour of the system, it is convenient to introduce new creation and annihilation operators. The corresponding procedure is composed of two steps:

1. introduction of the operators $d^{\dagger}_{\boldsymbol{p},s}$ and $d_{\boldsymbol{p},s}$ which create and annihilate quasi-particles in the case of free electrons;

2. introduction of the operators $a^{\dagger}_{\boldsymbol{p},s}$ and $a_{\boldsymbol{p},s}$ —which are obtained from $d^{\dagger}_{\boldsymbol{p},s}$ and $d_{\boldsymbol{p},s}$ by means of a Bogoliubov transformation— that diagonalize the hamiltonian (3.8).

STEP 1. The operators $d_{\boldsymbol{p},s}^\dagger$ and $d_{\boldsymbol{p},s}$ should describe the one-particle fluctuations with respect to the configuration of the Fermi sphere. Then $d_{\boldsymbol{p},s}^\dagger$ and $d_{\boldsymbol{p},s}$ are chosen in such a way that their vacuum state coincides with the free electrons ground state corresponding to the Fermi sphere. In the $T \to 0$ limit, the electron states with $p = |\boldsymbol{p}| < p_0$ are occupied whereas the states with $p = |\boldsymbol{p}| > p_0$ are empty, where

$$p_0 = \sqrt{2m\mu} \ . \tag{3.10}$$

Therefore $d_{\boldsymbol{p},s}^\dagger$ and $d_{\boldsymbol{p},s}$ are defined [25] by

$$
\begin{aligned}
d_{\boldsymbol{p},s}^\dagger &= \left\{ \begin{array}{ll} b_{-\boldsymbol{p},-s} & \text{for } p < p_0 \ ; \\ b_{\boldsymbol{p},s}^\dagger & \text{for } p > p_0 \ ; \end{array} \right. \\
d_{\boldsymbol{p},s} &= \left\{ \begin{array}{ll} b_{-\boldsymbol{p},-s}^\dagger & \text{for } p < p_0 \ ; \\ b_{\boldsymbol{p},s} & \text{for } p > p_0 \ , \end{array} \right.
\end{aligned} \tag{3.11}
$$

The creation operator $d_{\boldsymbol{p},s}^\dagger$ of a quasi-particle corresponds to the creation of a one-electron hole in the Fermi sphere if $|\boldsymbol{p}| < p_0$, and the creation of a one-electron occupied state if $|\boldsymbol{p}| > p_0$. As a result of the creation of a hole in the Fermi sphere, which corresponds to an electron state with momentum $-\boldsymbol{p}$ and spin component $-s$, the total momentum of the system increases by $\boldsymbol{p}$ and the total spin of the system increases by s. For this reason, when $p < p_0$ the quantum numbers of the operators $d_{\boldsymbol{p},s}^\dagger$ and $d_{\boldsymbol{p},s}$ are opposite with respect to the quantum numbers of $b_{\boldsymbol{p},s}^\dagger$ and $b_{\boldsymbol{p},s}$. The operators $d_{\boldsymbol{p},s}^\dagger$ and $d_{\boldsymbol{p},s}$ satisfy the canonical anticommutation relations

$$
\begin{aligned}
\{d_{\boldsymbol{p},s}, d_{\boldsymbol{q},r}^\dagger\} &= \delta_{sr} \frac{h^3}{V} \delta(\boldsymbol{p} - \boldsymbol{q}) \ , \\
\{d_{\boldsymbol{p},s}, d_{\boldsymbol{q},r}\} &= 0 = \{d_{\boldsymbol{p},s}^\dagger, d_{\boldsymbol{q},r}^\dagger\} \ .
\end{aligned} \tag{3.12}
$$

The operator number of quasi-particles $\widehat{N}_{qp}$ is given by $\widehat{N}_{qp} = \sum_{\boldsymbol{p},s} d_{\boldsymbol{p},s}^\dagger d_{\boldsymbol{p},s}$; $\widehat{N}_{qp}$ counts the number of holes inside the Fermi sphere plus the number of occupied states outside the Fermi sphere. The number of quasi-particles is not conserved, thus quasi-particles have vanishing chemical potential. In the $T \to 0$ limit, the number of quasi-particles vanishes. By using the relation $d_{\boldsymbol{p},s} d_{\boldsymbol{p},s}^\dagger = 1 - d_{\boldsymbol{p},s}^\dagger d_{\boldsymbol{p},s}$ and the definition (3.11), one finds

$$\sum_{\boldsymbol{p},s} \eta(p)\, b_{\boldsymbol{p},s}^\dagger b_{\boldsymbol{p},s} = \sum_{\boldsymbol{p},s} w(p)\, d_{\boldsymbol{p},s}^\dagger d_{\boldsymbol{p},s} + E_F(V,\mu) \ , \tag{3.13}$$

in which

$$w(p) = |\eta(p)| = \left| \frac{\boldsymbol{p}^2}{2m} - \mu \right| \ , \tag{3.14}$$

and

$$
\begin{aligned}
E_F(V,\mu) &= -\sum_{\boldsymbol{p},s}^{p<p_0} w(p) = -2 \sum_{\boldsymbol{p}}^{p<p_0} w(p) \\
&= -\frac{2V(2m)^{3/2}}{15\pi^2 \hbar^3} \mu^{5/2} \ .
\end{aligned} \tag{3.15}
$$

The gas of quasi-particles, which are associated with the operators (3.11), can also be used to compute the thermodynamic variables for a degenerate Fermi gas (as an alternative to the

Sommerfeld expansion). Note that, differently from the effective kinetic energy $\eta(p)$ of one electron, the kinetic energy $w(p)$ of one quasi-particle satisfies $w(p) \geq 0$.

STEP 2. By using the operators $d_{\boldsymbol{p},s}^{\dagger}$ and $d_{\boldsymbol{p},s}$, the hamiltonian (3.8) reads

$$
\begin{aligned}
H \quad \simeq \quad & \sum_{\boldsymbol{p},s} w(p)\, d_{\boldsymbol{p},s}^{\dagger} d_{\boldsymbol{p},s} + \sum_{\boldsymbol{p}} \left[\Delta_{\boldsymbol{p}}\, d_{\boldsymbol{p},+}^{\dagger} d_{-\boldsymbol{p},-}^{\dagger} + \Delta_{\boldsymbol{p}}\, d_{-\boldsymbol{p},-} d_{\boldsymbol{p},+} \right] \\
& + E_F(V,\mu) - \sum_{\boldsymbol{p}} \Delta_{\boldsymbol{p}} X_{\boldsymbol{p}} \, .
\end{aligned}
\tag{3.16}
$$

Since $d_{\boldsymbol{p},-}^{\dagger} d_{\boldsymbol{p},-} = 1 - d_{\boldsymbol{p},-} d_{\boldsymbol{p},-}^{\dagger}$, one can write

$$
\sum_{\boldsymbol{p},s} w(p)\, d_{\boldsymbol{p},s}^{\dagger} d_{\boldsymbol{p},s} = \sum_{\boldsymbol{p}} w(p) \left[d_{\boldsymbol{p},+}^{\dagger} d_{\boldsymbol{p},+} - d_{-\boldsymbol{p},-} d_{-\boldsymbol{p},-}^{\dagger} \right] + \sum_{\boldsymbol{p}} w(p) \, .
\tag{3.17}
$$

Thus the operator (3.16) can be written in the form

$$
H \simeq \sum_{\boldsymbol{p}} D_{\boldsymbol{p}}^{\dagger} \begin{pmatrix} w(p) & \Delta_{\boldsymbol{p}} \\ \Delta_{\boldsymbol{p}} & -w(p) \end{pmatrix} D_{\boldsymbol{p}} + E_F(V,\mu) - \sum_{\boldsymbol{p}} \Delta_{\boldsymbol{p}} X_{\boldsymbol{p}} + \sum_{\boldsymbol{p}} w(p) \, ,
\tag{3.18}
$$

where

$$
D_{\boldsymbol{p}} = \begin{pmatrix} d_{\boldsymbol{p},+} \\ d_{-\boldsymbol{p},-}^{\dagger} \end{pmatrix} \quad , \quad D_{\boldsymbol{p}}^{\dagger} = \begin{pmatrix} d_{\boldsymbol{p},+}^{\dagger} , d_{-\boldsymbol{p},-} \end{pmatrix} \, .
\tag{3.19}
$$

By means of the diagonalising matrix $M_{\boldsymbol{p}} \in SU(2)$ that satisfies the relation

$$
M_{\boldsymbol{p}}^{\dagger} \begin{pmatrix} w(p) & \Delta_{\boldsymbol{p}} \\ \Delta_{\boldsymbol{p}} & -w(p) \end{pmatrix} M_{\boldsymbol{p}} = \begin{pmatrix} \varepsilon(\boldsymbol{p}) & 0 \\ 0 & -\varepsilon(\boldsymbol{p}) \end{pmatrix} \, ,
\tag{3.20}
$$

in which

$$
\varepsilon(\boldsymbol{p}) = \sqrt{w^2(p) + \Delta_{\boldsymbol{p}}^2} \, ,
\tag{3.21}
$$

one can introduce new creation and annihilation operators $a_{\boldsymbol{p},s}^{\dagger}$ and $a_{\boldsymbol{p},s}$ according to

$$
\begin{pmatrix} a_{\boldsymbol{p},+} \\ a_{-\boldsymbol{p},-}^{\dagger} \end{pmatrix} = M_{\boldsymbol{p}}^{\dagger} \cdot D_{\boldsymbol{p}} \quad , \quad \begin{pmatrix} a_{\boldsymbol{p},+}^{\dagger} , a_{-\boldsymbol{p},-} \end{pmatrix} = D_{\boldsymbol{p}}^{\dagger} \cdot M_{\boldsymbol{p}} \, .
\tag{3.22}
$$

One then obtains

$$
\begin{aligned}
\sum_{\boldsymbol{p}} D_{\boldsymbol{p}}^{\dagger} \begin{pmatrix} w(p) & \Delta_{\boldsymbol{p}} \\ \Delta_{\boldsymbol{p}} & -w(p) \end{pmatrix} D_{\boldsymbol{p}} \quad = \quad & \sum_{\boldsymbol{p}} \varepsilon(\boldsymbol{p}) \left[a_{\boldsymbol{p},+}^{\dagger} a_{\boldsymbol{p},+} - a_{-\boldsymbol{p},-} a_{-\boldsymbol{p},-}^{\dagger} \right] \\
= \quad & \sum_{\boldsymbol{p},s} \varepsilon(\boldsymbol{p})\, a_{\boldsymbol{p},s}^{\dagger} a_{\boldsymbol{p}s} - \sum_{\boldsymbol{p}} \varepsilon(\boldsymbol{p}) \, .
\end{aligned}
\tag{3.23}
$$

By using the operators $a_{\boldsymbol{p},s}^{\dagger}$ and $a_{\boldsymbol{p},s}$, the effective hamiltonian (3.18) assumes the diagonal form

$$
H \simeq \sum_{\boldsymbol{p},s} \varepsilon(\boldsymbol{p})\, a_{\boldsymbol{p},s}^{\dagger} a_{\boldsymbol{p}s} + \mathcal{E}_0 \, ,
\tag{3.24}
$$

8

where

$$\mathcal{E}_0 = \sum_{\boldsymbol{p}} \left[w(p) - \varepsilon(\boldsymbol{p}) - \Delta_{\boldsymbol{p}} X_{\boldsymbol{p}} \right] + E_F(V, \mu) \; . \tag{3.25}$$

The operators $a_{\boldsymbol{p},s}^{\dagger}$ and $a_{\boldsymbol{p},s}$ verify

$$\begin{aligned} \{a_{\boldsymbol{p},s}\,, a_{\boldsymbol{q},r}^{\dagger}\} &= \delta_{sr} \frac{h^3}{V} \delta(\boldsymbol{p} - \boldsymbol{q}) \quad , \\ \{a_{\boldsymbol{p},s}\,, a_{\boldsymbol{q},r}\} &= 0 = \{a_{\boldsymbol{p},s}^{\dagger}\,, a_{\boldsymbol{q},r}^{\dagger}\} \; , \end{aligned} \tag{3.26}$$

and represent the creation and annihilation operators for quasi-particles (the so-called bogolons) with dispersion relation $\varepsilon(\boldsymbol{p})$. The grand partition function (3.3) is given by

$$\mathcal{Q}(T, V, \mu) = \mathrm{Tr} \left[e^{-H/kT} \right] = e^{-\mathcal{E}_0/kT} \prod_{\boldsymbol{p},s} \left[1 + e^{-\varepsilon(\boldsymbol{p})/kT} \right] \; , \tag{3.27}$$

and then the grand potential Ω for the system of conducting electrons turns out to be

$$\Omega(T, V, \mu) = -kT \sum_{\boldsymbol{p},s} \ln \left[1 + e^{-\varepsilon(\boldsymbol{p})/kT} \right] + \mathcal{E}_0 \; . \tag{3.28}$$

The introduction of Step 1 clarifies the nature of the bogolons and the resulting formalism is consistent with the vanishing of the bogolon chemical potential. Note that, if the Bogoliubov transformation is directly applied to the creation and annihilation operators $b_{\boldsymbol{p},s}^{\dagger}$ and $b_{\boldsymbol{p},s}$ of the electrons, one finds sign ambiguities [27] in the energy spectrum. The method that has been presented here has the advantage of avoiding these ambiguities. By the way, the correct solution of these ambiguities is rather nontrivial. Because, if the electron effective energy $\eta(p)$ takes the place of $w(p)$, the thermodynamic consistency requires that the right sign of the dispersion relation should be $+\varepsilon(\boldsymbol{p})$ when $|\boldsymbol{p}| > p_0$ and $-\varepsilon(\boldsymbol{p})$ when $|\boldsymbol{p}| < p_0$. The correct value (3.25) of the energy $\mathcal{E}_0$ of the vacuum of the quasi-particles is a fundamental ingredient in the following discussions in Section 4 and Section 5. Group properties of the quasi-particles vacuum and features of the solution of the gap equation have been discussed, for instance, in Ref.[29, 30, 31].

In order to complete the derivation of Ω, one has to impose the statistical self-consistency of the approximation (3.8), in which the mean values (3.6) have been used. Let us briefly recall the method which is usually presented in literature for this purpose. The mean values (3.6) can be related with the mean values of the corresponding operators defined in terms of $a_{\boldsymbol{p},s}^{\dagger}$ and $a_{\boldsymbol{p},s}$. Since the quasi-particles created and annihilated by $a_{\boldsymbol{p},s}^{\dagger}$ and $a_{\boldsymbol{p},s}$ behave as free particles, the only nontrivial mean value is given by $\langle a_{\boldsymbol{p},s}^{\dagger} a_{\boldsymbol{p},s} \rangle = n_{\boldsymbol{p}}$, where the quasi-particle distribution $n_{\boldsymbol{p}}$ is shown in equation (2.5). In this way, by using the definition (3.9), one can obtain the gap equation [3, 4, 27, 28, 32]

$$1 = \frac{U_0}{V} {\sum_{\boldsymbol{p}}}' \frac{1}{2\varepsilon(\boldsymbol{p})} \, \mathrm{Th} \left[\varepsilon(\boldsymbol{p})/2kT \right] \; , \tag{3.29}$$

where ${\sum_{\boldsymbol{p}}}'$ denotes the integral in the neighbourhood of the surface of the Fermi sphere which is specified by the condition $\left| (\boldsymbol{p}^2/2m) - \mu \right| \leq \hbar \omega_D$. In the next section, an alternative derivation of the gap equation will be produced.

4 Thermodynamic consistency and the gap equation

From the definition (3.9) and the experimental fact that the superconducting electrons belong to a neighbourhood of the Fermi surface, where $U_{\boldsymbol{p},\boldsymbol{q}} \simeq -U_0/V$, it follows that one can put

$$\Delta_p = \begin{cases} \Delta & \text{for} \ \ \left|(\boldsymbol{p}^2/2m) - \mu\right| \leq \hbar\omega_D \,; \\[2ex] 0 & \text{otherwise;} \end{cases} \tag{4.1}$$

and then

$$-\sum_{\boldsymbol{p}} \Delta_p X_p = \frac{V}{U_0}\Delta^2 \,. \tag{4.2}$$

Let us now consider the expression (3.28) and let us assume, for the moment, that the value Δ of the gap is a free undeterminate which is not specified by the gap equation; one has

$$\Omega(T,V,\mu) = -2kT\sum_{\boldsymbol{p}} \ln\left[1 + e^{-\varepsilon(\boldsymbol{p})/kT}\right] + \mathcal{E}_0 \,, \tag{4.3}$$

where

$$\mathcal{E}_0 = \sum_{\boldsymbol{p}} \left[\,\left|(\boldsymbol{p}^2/2m) - \mu\right| - \varepsilon(\boldsymbol{p})\right] + \frac{V}{U_0}\Delta^2 + E_F(V,\mu) \,. \tag{4.4}$$

Let us denote by $\mathcal{B}$ the neighbourhood of the Fermi surface which is defined by the condition $\left|(\boldsymbol{p}^2/2m) - \mu\right| \leq \hbar\omega_D$. Then

$$\varepsilon(\boldsymbol{p}) = \begin{cases} \left[\left|(\boldsymbol{p}^2/2m) - \mu\right|^2 + \Delta^2\right]^{1/2} & \text{for} \ \ \boldsymbol{p} \in \mathcal{B}; \\[2ex] \left|(\boldsymbol{p}^2/2m) - \mu\right| & \text{otherwise.} \end{cases} \tag{4.5}$$

Since Ω is the thermodynamic potential associated with the variables (T,V,μ), for fixed (T,V,μ) the system tends to minimize Ω. So, in the equilibrium state, the value $\widetilde{\Delta}$ of the gap can be obtained by imposing the variational condition

$$\left(\frac{\partial\Omega}{\partial\Delta}\right)_{T,V,\mu}\bigg|_{\Delta=\widetilde{\Delta}} = 0 \,. \tag{4.6}$$

Since

$$\frac{\partial\varepsilon(\boldsymbol{p})}{\partial\Delta} = \begin{cases} \Delta/\varepsilon(\boldsymbol{p}) & \text{when} \ \ \left|(\boldsymbol{p}^2/2m) - \mu\right| \leq \hbar\omega_D \,; \\[2ex] 0 & \text{otherwise,} \end{cases} \tag{4.7}$$

one finds

$$\frac{\partial}{\partial\Delta}\left\{-2kT\sum_{\boldsymbol{p}} \ln\left[1 + e^{-E_{\boldsymbol{p}}/kT}\right]\right\} = \Delta\sum_{\boldsymbol{p}}' \frac{1}{\varepsilon(\boldsymbol{p})}\frac{2}{e^{\varepsilon(\boldsymbol{p})/kT} + 1} \,. \tag{4.8}$$

Moreover

$$\frac{\partial}{\partial\Delta}\sum_{\boldsymbol{p}} \left[\left|(\boldsymbol{p}^2/2m) - \mu\right| - \varepsilon(\boldsymbol{p})\right] = -\Delta\sum_{\boldsymbol{p}}' \frac{1}{\varepsilon(\boldsymbol{p})} \,, \tag{4.9}$$

and

$$\frac{\partial}{\partial \Delta}\left(\frac{V}{U_0}\Delta^2\right) = \Delta \frac{2V}{U_0} .$$ (4.10)

Equations (4.8)-(4.10) imply

$$\frac{\partial \Omega}{\partial \Delta} = \Delta \left\{ \sum_{\boldsymbol{p}}' \frac{1}{\varepsilon(\boldsymbol{p})} \left[\frac{2}{e^{\varepsilon(\boldsymbol{p})/kT}+1} - 1\right] + \frac{2V}{U_0} \right\} .$$ (4.11)

By using the identity

$$\frac{2}{e^{\varepsilon(\boldsymbol{p})/kT}+1} - 1 = -\mathrm{Th}(\varepsilon(\boldsymbol{p})/2kT) ,$$ (4.12)

the minimum condition (4.6) turns out to be equivalent to (apart from the trivial solution)

$$1 = \frac{U_0}{V}\sum_{\boldsymbol{p}}' \frac{1}{2\varepsilon(\boldsymbol{p})} \mathrm{Th}(\varepsilon(\boldsymbol{p})/2kT) ,$$ (4.13)

which coincides precisely with the gap equation (3.29). In what follows, the value of the gap satisfying equation (4.13) will be simply denoted by $\Delta = \Delta(T, \mu)$.

To sum up, the grand potential Ω for the electrons system takes the form

$$\Omega(T, V, \mu) = F_q(T, V; \Delta(T, \mu)) + \mathcal{E}_0(V, \mu; \Delta(T, \mu)) ,$$ (4.14)

where F_q denotes the free energy for the gas of quasi-particles, with dispersion relation $\varepsilon(\boldsymbol{p})$ shown in equation (4.5), and $\mathcal{E}_0$ of equation (4.4) represents the vacuum energy of the quasi-particles. The value $\Delta(T, \mu)$ of the gap corresponds to a minimum of Ω for fixed (T, V, μ).

Let us now consider the issue of the thermodynamic consistency of the result (4.14). The starting expression (3.3) is thermodynamically consistent, because the dependence of the grand partition function on the macroscopic variables (T, V, μ) is the standard dependence of statistical physics. However, when the dependence of the gap on the variables T and μ has been introduced, $\Delta = \Delta(T, \mu)$, the standard rules of statistical physics have been modified. Now, the dependence of Ω on the variables (T, V, μ) consists of two parts:

- the (thermodynamically consistent) explicit dependence on (T, V, μ) displayed in expressions (4.3)-(4.5);

- the indirect dependence on (T, μ) through $\Delta = \Delta(T, \mu)$.

Let us distinguish these two possibilities by means of the notation

$$\Omega = \Omega(T, V, \mu; \Delta(T, \mu)) .$$ (4.15)

When computing the derivatives of Ω one finds, for instance,

$$\frac{\partial \Omega}{\partial T} = \left(\frac{\partial \Omega}{\partial T}\right)_\Delta + \left(\frac{\partial \Omega}{\partial \Delta}\right)_T \frac{\partial \Delta}{\partial T} .$$ (4.16)

But since the value of the gap minimizes Ω, the term $(\partial \Omega/\partial \Delta)_T$ vanishes, and then the derivative $\partial \Delta/\partial T$ does not contribute to $\partial \Omega/\partial T$. Therefore, only the thermodynamically consistent

dependence of Ω on (T, V, μ) really contributes to the derivates. This means that the Maxwell relations associated with Ω are satisfied.

Let us now consider a generic thermodynamic potential which is derived from Ω by means of appropriate Legendre transformations. As far as the variable Δ is concerned, the so-called *theorem of small increments* [33] takes the form

$$0 = \left(\frac{\partial \Omega}{\partial \Delta}\right)_{T,V,\mu} = \left(\frac{\partial F}{\partial \Delta}\right)_{T,V,N} = \left(\frac{\partial U}{\partial \Delta}\right)_{V,S,N} = \cdots , \tag{4.17}$$

and states that Δ really corresponds to a stationary point of each potential (provided the corresponding set of thermodynamic variables is kept fixed). Consequently, when constructing the thermodynamic relations by means of the first derivatives of the potentials, Δ effectively behaves like a constant term, and does not alter the Maxwell relations. Thus, because of the validity of the gap equation, the quasi-particles description of the systems, which is given —in the low temperature limit— by the grand potential (4.14), is perfectly consistent with the validity of the standard thermodynamic relations.

This example of superconducting electrons is in agreement with the Landau principle, which states that the value of any order parameter entering a given thermodynamic potential actually corresponds to a stationary point of the same potential, with the appropriate thermodynamic variables held fixed.

5 Thermodynamic potentials

Quite often, the complete expression (4.14) of the grand potential and, in particular, the complete expression (4.4) of the energy $\mathcal{E}_0$ are not explicitly displayed in literature. In certain cases, the combination $\sum_{\boldsymbol{p}} [w(p) - \varepsilon(\boldsymbol{p}) - \Delta_{\boldsymbol{p}} X_{\boldsymbol{p}}]$ is reported, however the term $E_F(V, \mu)$ is missing. Consequently, in these cases the partial derivatives of Ω with respect to V and μ are invalidated and thus the deduction of the thermodynamic potentials as functions of the variables (T, V, N) becomes problematic. Usually, the explicit derivation of the general dependence of the superconducting thermodynamic potentials on (T, V, N) represents a rather laborious task. So, let us now derive from equation (4.14) a few thermodynamic potentials as functions of (T, V, N) when $T < T_c$ in the low temperature limit. Let us compute, in particular, how the chemical potential gets modified by the superconducting phase transition and how μ depends on the electron density. The dependence of μ on (T, V, N) is indeed the fundamental ingredient for the determination of the consistent thermodynamic potentials.

In the $T \to 0$ limit, the quasi-particles distribution is mainly concentrated around the minimum of the energy spectrum. The energy (3.21) of a single quasi-particle can be written as $\varepsilon = \varepsilon_w = \sqrt{w^2 + \Delta^2}$ and, in a neighbourhood of the minimum $w = 0$, it can be approximated as

$$\varepsilon_w = \sqrt{w^2 + \Delta^2} \simeq \Delta + \frac{w^2}{2\Delta} . \tag{5.1}$$

Accordingly, in the computations of F_q and of $\mathcal{E}_0$ the integral in momentum space is effectively dominated by the integration in a neighbourhood of the surface of the Fermi sphere and it can be written as

$$\sum_{\boldsymbol{p}} \to \frac{V(2m)^{3/2}}{2\pi^2 \hbar^3} \sqrt{\mu} \int dw . \tag{5.2}$$

The grand potential (4.14) reads

$$
\begin{aligned}
\Omega(T, V, \mu) \quad \simeq \quad & -VkT\frac{(2m)^{3/2}}{\pi^2\hbar^3}\mu^{1/2}\int_0^\infty dw \, \ln\left[1 + e^{-\varepsilon_w/kT}\right] \\
& +V\frac{(2m)^{3/2}}{2\pi^2\hbar^3}\mu^{1/2}\int_0^{\hbar\omega_D} dw \, [w - \varepsilon_w] \\
& +\frac{V}{U_0}\Delta^2 - \frac{2V(2m)^{3/2}}{15\pi^2\hbar^3}\mu^{5/2} \; .
\end{aligned}
\tag{5.3}
$$

In the thermodynamic limit, the statistical mean value N of the number of electrons is specified by the relation $N = -\partial\Omega/\partial\mu$, which takes the form

$$
\begin{aligned}
\frac{3\pi^2\hbar^3}{(2m)^{3/2}}\frac{N}{V} \quad \simeq \quad & \mu^{3/2} + \frac{3kT}{2\mu^{1/2}}\int_0^\infty dw \, \ln\left[1 + e^{-\varepsilon_w/kT}\right] \\
& -\frac{3}{4\mu^{1/2}}\int_0^{\hbar\omega_D} dw \, [w - \varepsilon_w] \; .
\end{aligned}
\tag{5.4}
$$

In the low temperature limit one has $\Delta/\varepsilon_F \ll 1$ and $(kT/\varepsilon_F) \ll 1$, where ε_F denotes the Fermi energy

$$
\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{N}{V}\right)^{2/3}\left(3\pi^2\right)^{2/3} \; .
\tag{5.5}
$$

So, the chemical potential can be determined perturbatively in powers of $(kT/\varepsilon_F) \ll 1$ and $\Delta/\varepsilon_F \ll 1$ from equation (5.4); to lowest non-trivial orders one finds

$$
\mu \simeq \varepsilon_F - \frac{kT}{\varepsilon_F}\int_0^\infty dw \, \ln\left[1 + e^{-\varepsilon_w/kT}\right] + \frac{1}{2\varepsilon_F}\int_0^{\hbar\omega_D} dw \, [w - \varepsilon_w] \; .
\tag{5.6}
$$

This relation gives the desired expression for the chemical potential. It should be noted that, in addition to the quasi-particles contributions to μ, the last term on the right-hand-side of equation (5.6) describes precisely the effects of the quasi-particles vacuum rearrangement — that takes place at the critical point— on the chemical potential. The free energy F is given by $F = \Omega + N\mu$,

$$
\begin{aligned}
F(T, V, N) \quad \simeq \quad & -\frac{3NkT}{\varepsilon_F}\int_0^\infty dw \, \ln\left[1 + e^{-\varepsilon_w/kT}\right] + \frac{3}{5}N\varepsilon_F \\
& +\frac{3N}{2\varepsilon_F}\int_0^{\hbar\omega_D} dw \, [w - \varepsilon_w] + \frac{V}{U_0}\Delta^2 \; .
\end{aligned}
\tag{5.7}
$$

The entropy $S = -\partial F/\partial T$ turns out to be

$$
\begin{aligned}
S(T, V, N) \quad \simeq \quad & \frac{3Nk}{\varepsilon_F}\int_0^\infty dw \, \ln\left[1 + e^{-\varepsilon_w/kT}\right] \\
& +\frac{3N}{T\varepsilon_F}\int_0^\infty dw \, \frac{\varepsilon_w}{e^{\varepsilon_w/kT} + 1} \; ,
\end{aligned}
\tag{5.8}
$$

and coincides with the entropy of the gas of quasi-particles, as it must be. Finally, the internal energy $U = F + TS$ is given by

$$U(T, V, N) \simeq \frac{3N}{\varepsilon_F} \int_0^\infty dw \, \frac{\varepsilon_w}{e^{\varepsilon_w/kT} + 1} + \frac{3}{5} N \varepsilon_F$$
$$+ \frac{3N}{2\varepsilon_F} \int_0^{\hbar\omega_D} dw \, [w - \varepsilon_w] + \frac{V}{U_0} \Delta^2 . \qquad (5.9)$$

The consequences of expressions (5.3)-(5.9) are in agreement with the known results [3, 4, 13, 27, 34, 35] on superconductivity. As a check, let us compute the condensation energy. The energy of the quasi-particles gas can be obtained by means of the gaussian approximation

$$\frac{3N}{\varepsilon_F} \int_0^\infty dw \, \frac{\varepsilon_w}{e^{\varepsilon_w/kT} + 1} \simeq \frac{3N\Delta}{2\varepsilon_F} e^{-\Delta/kT} \sqrt{2\pi\Delta kT} ; \qquad (5.10)$$

this energy contribution vanishes in the $T \to 0$ limit. Since $\Delta/\hbar\omega_D \ll 1$, one finds

$$\int_0^{\hbar\omega_D} dw \, [w - \varepsilon_w] \simeq -\tfrac{1}{4}\Delta^2 + \tfrac{1}{2}\Delta^2 \ln(\Delta/2\hbar\omega_D) . \qquad (5.11)$$

In the $T \to 0$ limit, the value of Δ is specified by the gap equation (4.13); in particular, when $(3NU_0/4V\varepsilon_F) \ll 1$, one obtains [3, 4, 13]

$$(\Delta/2\hbar\omega_D) \simeq e^{-(4V\varepsilon_F/3NU_0)} . \qquad (5.12)$$

By means of relation (5.12), one gets

$$\frac{3N}{2\varepsilon_F} \int_0^{\hbar\omega_D} dw \, [w - \varepsilon_w] + \frac{V}{U_0} \Delta^2 \simeq -\frac{3N\Delta^2}{8\varepsilon_F} . \qquad (5.13)$$

Within the considered approximations, the value E_C of the condensation energy is obtained by subtracting the energy of a free fermions gas at $T = 0$ from the system energy $U(T = 0, V, N)$. Since the energy of a free electrons gas in the Fermi sphere is equal to $(3/5)N\varepsilon_F$, the condensation energy E_C turns out to be

$$E_C = U(T = 0, V, N) - \frac{3}{5} N \varepsilon_F = -\frac{3N\Delta^2(T=0)}{8\varepsilon_F} , \qquad (5.14)$$

which is in agreement with the results of the alternative derivations presented in [3, 4, 13].

6 Summary and conclusions

In the Bogoliubov-Valatin approach, it has been shown that the relevant variables —that must be considered for the computation of the thermodynamic potentials— are associated with the energy fluctuations of the system around the Fermi sphere configuration. By means of a Bogoliubov transformation in these variables one gets the expression of the quasi-particles vacuum energy, which is the fundamental ingredient in the construction of the grand potential $\Omega(T, V, \mu)$ for the superconducting electrons. The value of the gap corresponds to a minimum of Ω and the

gap equation precisely represents the stationarity condition. When the gap equation is satisfied, Ω and the thermodynamic potentials that are derived from Ω satisfy the Maxwell relations. The expressions of the thermodynamic potentials as functions of the (T, V, N) variables have been derived. The dependence of the chemical potential on the electron density and the effects of the superconducting phase transition on the chemical potential have been computed in the low energy limit. As a final check, a derivation of the condensation energy from $\Omega(T, V, \mu)$ has been presented.

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