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Multiple phases in a new statistical boson–fermion model of superconductivity

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Abstract

We apply a new statistical complete boson–fermion model (CBFM) to describe superconductivity with arbitrary departure from the perfect two-electron (2e) and two-hole (2h) Cooper pair (CP) symmetry to which BCS theory is restricted. The model is complete in that it accounts for both 2h and 2e CPs. In special cases the CBFM reduces to all the main statistical continuum models of superconductivity. From it four stable thermodynamic phases emerge around the BCS state, a *normal* and three stable Bose–Einstein condensed phases of which one is *mixed* (with both CP types) and two pure. Critical temperatures T_c for the new pure phases *rise* as one departs from the mixed BCS state, and can result in substantially higher T_c 's than with BCS theory for moderate departures from perfect 2e/2h CP symmetry.

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1. Introduction

Statistical boson–fermion (BF) models of superconductivity go back to the mid-1950s [1–3] pre-dating even the BCS-Bogoliubov theory [4,5]. Although BCS theory only contemplates the presence of Cooper “correlations” between fermion charge carriers,

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BF models [1–3,6–16] posit the existence of real bosonic Cooper pairs (CPs). See also Refs. [17–27]. Such paired charge carriers have been observed in magnetic flux quantization experiments on elemental as well as cuprate superconductors, although there seems to be no experiment yet that distinguishes between electron (e) and hole (h) CPs. With one exception [15], however, BF models neglect the effect of 2h CPs (formulated on an equal footing with 2e CPs) to give a CBFM consisting of unpaired fermions (both e and h) coexisting with both bosonic CP species. Previous BF models account, of course, for eh symmetry of individual fermions arising as a trivial consequence of Fermi–Dirac statistics. Besides this obvious symmetry, the CBFM accounts also for eh CP symmetry as we now introduce a 2h-CP which is distinct from, and kinematically independent of, a 2e-CP since their Bose commutation relations involve a relative sign change, in sharp contrast with e or h fermions whose Fermi anticommutation relations do not.

All the main statistical theories of superconductivity emerge as special cases of the CBFM [15]. When the number of 2e- and 2h-CPs are identically equal it leads to: (i) the BCS theory for weak coupling which in turn forces the fermionic chemical potential to equal the Fermi energy. When 2h-CPs are neglected entirely it gives: (ii) the Friedberg–Lee Bose–Einstein condensation (BEC) theory [8,9] of a BF charged gas, as well as: (iii) an ideal BF model [26,27] predicting nonzero BEC-like T_c 's even in 2D, and finally: (iv) the ordinary BEC T_c formula.

The unique but mysterious role played by holes in superconductivity in general has been emphasized, e.g. by Hirsch [28] among others, through some remarkable facts. For example, (a) over 80% of all superconducting elements have positive Hall coefficients (meaning hole charge carriers in the normal state); (b) over 90% of nonsuperconducting metallic, nonmagnetic elements have electron charge carriers; (c) of the cuprate superconductors those that are hole-doped have transition temperatures T_c about six times higher than electron-doped ones; and (d) in fullerite (an fcc crystal of C_{60} fullerenes) T_c is now almost three times higher with hole rather than electron doping, as recently observed [29] with the so-called “field-effect transistor” technique of injecting holes. A many-body statistical formalism that departs from perfect eh symmetry is thus clearly needed. And it is tempting to visualize the vital role that hole CPs might come to play in superconductivity—as suggested by decisive role of individual holes in the 1950s in semiconductors [30], without which the transistor might not have been invented let alone applied. This paper is a step towards understanding their full role in superconductivity, particularly as regards the 2h CP component, through purely statistical considerations.

Indeed, holes have a dramatic effect in the elementary CP problem (where they were originally neglected) which gives [31] a negative-energy, stationary (i.e., infinite-lifetime) two-fermion bound-state. If electrons and holes are treated simultaneously through a Bethe–Salpeter equation in the ideal Fermi gas (IFG) ground-state about which the CPs are defined, the resulting energy is purely imaginary [5, p. 44]; [32, Section 33]—implying an obvious instability. The original CP problem is thus meaningless if particles are taken on an equal footing with holes as consistency would demand. However, a similar Bethe–Salpeter treatment, not about the IFG but about the BCS ground-state, yields [33] real (but positive, as with a “quasi-bound-state in the

continuum”) 2e- and 2h-CP energies, along with an imaginary part implying a finite lifetime—thus vindicating the CP problem in a very physical way.

The BCS-Bogoliubov (BCS-B) microscopic statistical theory of superconductivity [4,5] implies perfect eh symmetry in that 2e and 2h Cooper *correlations* occur in equal proportions. This theory emerges [15] as a special case of the CBFM consisting of CPs as *explicit* individual composite 2e and 2h bosons, kinematically independent of each other, and of the unpaired electrons and holes, in a BF gas mixture that can suffer a BEC (-like) transition at sufficiently low temperatures.

The purpose of this paper is twofold: (a) to numerically exhibit within the CBFM the phase diagram in the vicinity of the BCS-B state at $T = T_c$ which turns out to be surrounded by the normal (i.e., ideal, noninteracting BF) phase as well as three superconducting BEC ones of which the two pure phases are higher- T_c ones; and (b) to prove that BCS-B theory follows from the CBFM for perfect eh CP symmetry in the limit of weak interaction, not only from the gap equation as shown in Ref. [15] but also from the condensation energy *and* from at least two dimensionless universal ratios.

To simplify the dynamical aspect of the problem we assume that both 2e- and 2h-CP condensed bosons together with the unpaired electrons and holes undergo the elementary processes



where $(2e)_{cond}$ and $(2h)_{cond}$ are the 2e- and 2h-CPs in their BE condensates. We designate as *crossed* the two-fermion interaction (1) [6–10,13,15,16] present in these reactions to distinguish it from the more familiar *direct* four-fermion interaction in the electron–electron scattering reaction



The latter involves some fixed inter-fermion potential as, e.g., in both Refs. [4,5] where an electron–phonon mechanism is modeled by a separable potential with a cutoff related to the Debye frequency. Such a dynamical coupling was recently seen [34] in angle-resolved photoemission spectroscopy to strongly influence the electron dynamics *also* in high-temperature cuprate superconductors. Ref. [6] refers to (1) as a “hybridization” interaction, and appears to be the first time it is used, but *without* 2h-CPs and hence unrelated to BCS theory which the CBFM naturally includes as a special case; Refs. [8,9] refer to (1) and (2) as the “s- and t-channel” interactions, respectively.

2. Complete boson–fermion model

The statistical CBFM was defined [15] as consisting of unpaired electrons and holes (as unpaired fermions) plus two different kinds of kinematically independent 2e- and 2h-CP bosons which interact in a specific way with the unpaired fermions. A common misconception is that CPs are not bosons because they are too extended in size, and indeed overlap severely, as a result of which their creation and annihilation operators for

fixed momentum wavevectors \mathbf{k}_1 and \mathbf{k}_2 [or, alternatively, fixed relative $\mathbf{k} \equiv \frac{1}{2}(\mathbf{k}_1 - \mathbf{k}_2)$ and total or center-of-mass $\mathbf{K} \equiv \mathbf{k}_1 + \mathbf{k}_2$ wavevectors] are known not [35, p. 38] to obey the usual Bose commutation relations. However, indefinitely large occupation in a state of given \mathbf{K} , needed to ensure the BE distribution in turn required for BEC, indeed occurs (see Ref. [25, p. 181ff]) for the objects whose energy $E_{\pm}(K)$ [see (3)] depends only on \mathbf{K} but *not* on \mathbf{k} . For example, with the BCS model interaction (Ref. [36, see esp. Fig. 1]) there will be, for *any* coupling and in the thermodynamic limit, indefinitely many values of the relative momenta \mathbf{k} for a given \mathbf{K} . Hence, CPs thus formed do in fact obey the BE distribution.

The CBFM is described by $H = H_0 + H_{int}$ where the unperturbed Hamiltonian H_0 corresponds to an ideal (i.e., noninteracting) gas mixture of fermions plus both types of CPs, 2e and 2h, namely

$$H_0 = \sum_{\mathbf{k}_1, s_1} \varepsilon_{\mathbf{k}_1} a_{\mathbf{k}_1, s_1}^+ a_{\mathbf{k}_1, s_1} + \sum_{\mathbf{K}} E_+(K) b_{\mathbf{K}}^+ b_{\mathbf{K}} - \sum_{\mathbf{K}} E_-(K) c_{\mathbf{K}}^+ c_{\mathbf{K}}, \quad (3)$$

where $a_{\mathbf{k}_1, s_1}^+ / a_{\mathbf{k}_1, s_1}$ are creation/annihilation operators for fermions and similarly $b_{\mathbf{K}}^+ / b_{\mathbf{K}}$ and $c_{\mathbf{K}}^+ / c_{\mathbf{K}}$ for 2e- and 2h-CP bosons, respectively. Also, $\varepsilon_{\mathbf{k}} \equiv \hbar^2 k^2 / 2m$ are the electron while $E_{\pm}(K)$ are the 2e- and 2h-CP energies. The interaction Hamiltonian H_{int} contains two-fermion/one-boson interaction vertices, each between unpaired electrons (subindex +) [or holes (subindex -)] and the BE-condensed 2e- and 2h-CPs allowed in the system of size L , namely

$$H_{int} = L^{-3/2} \sum_{\mathbf{k}, \mathbf{K}} f_+(k) \{ a_{\mathbf{k}+\frac{1}{2}\mathbf{K}, \uparrow}^+ a_{-\mathbf{k}+\frac{1}{2}\mathbf{K}, \downarrow}^+ b_{\mathbf{K}} + a_{-\mathbf{k}+\frac{1}{2}\mathbf{K}, \downarrow} a_{\mathbf{k}+\frac{1}{2}\mathbf{K}, \uparrow} b_{\mathbf{K}}^+ \} \\ + L^{-3/2} \sum_{\mathbf{k}, \mathbf{K}} f_-(k) \{ a_{\mathbf{k}+\frac{1}{2}\mathbf{K}, \uparrow}^+ a_{-\mathbf{k}+\frac{1}{2}\mathbf{K}, \downarrow}^+ c_{\mathbf{K}}^+ + a_{-\mathbf{k}+\frac{1}{2}\mathbf{K}, \downarrow} a_{\mathbf{k}+\frac{1}{2}\mathbf{K}, \uparrow} c_{\mathbf{K}} \}. \quad (4)$$

Note that H_{int} is reminiscent of the Fröhlich (or Dirac QED) interaction Hamiltonian involving two fermion and one boson operators—but with two types of CPs instead of phonons (or photons). Just as these two interaction Hamiltonians are the most natural ones to employ in a many-electron/phonon (or photon) system, one can conjecture the same of (4) for the CBFM system under study. Indeed, it has already been used by many authors [6–10,13,15,16]. In contrast with the Fröhlich or Dirac hamiltonians, however, (4) does not conserve the number of individual electrons. The different species in the CBFM are all embedded in a uniform background of positive charge ensuring charge neutrality, and which furnishes the usual screening of the Coulomb interactions between species.

Following the Bogoliubov [37] recipe, exact in the thermodynamic limit, we allow for a possible BEC of the 2e- and 2h-CP bosons with $\mathbf{K} = 0$ by replacing everywhere both creation and annihilation Bose operators b_0^+, b_0 for 2e-CPs by the c-number $\sqrt{N_0}$ (N_0 being the number of BE-condensed 2e-CPs, i.e., with $\mathbf{K} = 0$) and Bose operators c_0^+, c_0 for 2h-CPs by another c-number $\sqrt{M_0}$ (M_0 being the number of BE-condensed 2h-CPs also with $\mathbf{K} = 0$). Note that this recipe goes *beyond* mean-field theory since one can show that the replacement implies *no* approximation provided one imposes the conditions of thermodynamic equilibrium, (17) below.

Neglecting interactions between unpaired electrons and *excited* or $\mathbf{K} \neq 0$ CP bosons, but accounting fully as in Refs. [6–10,13,15,16] for interactions between condensed bosons (with $\mathbf{K} = 0$) and unpaired fermions, the relevant dynamical operator $\hat{H} - \mu\hat{N}$ is then approximately given by

$$\begin{aligned} \hat{H} - \mu\hat{N} \simeq & \sum_{\mathbf{k},s} [\varepsilon_k - \mu] a_{\mathbf{k},s}^+ a_{\mathbf{k},s} \\ & + [E_+(0) - 2\mu] N_0 + \sum_{\mathbf{K} \neq 0} [E_+(K) - 2\mu] b_{\mathbf{K}}^+ b_{\mathbf{K}} \\ & + [2\mu - E_-(0)] M_0 + \sum_{\mathbf{K} \neq 0} [2\mu - E_-(K)] c_{\mathbf{K}}^+ c_{\mathbf{K}} \\ & + \sum_{\mathbf{k}} [\sqrt{n_0} f_+(k) + \sqrt{m_0} f_-(k)] (a_{\mathbf{k}\uparrow}^+ a_{-\mathbf{k}\downarrow}^+ + a_{-\mathbf{k}\downarrow} a_{\mathbf{k}\uparrow}) . \end{aligned} \quad (5)$$

Here \hat{N} is the operator associated with the total number of fermions in the system, including unpaired, i.e., individual as well as paired fermions, while $n_0 \equiv N_0/L^3$ and $m_0 \equiv M_0/L^3$ are the number densities of condensed 2e- and 2h-CPs, respectively. For the kinetic energies $E_{\pm}(K)$ of 2e- and 2h-CPs with momentum $\hbar\mathbf{K}$ we assume the quadratic dispersion relations $E_{\pm}(K) = E_{\pm}(0) \pm \hbar^2 K^2/4m$ as in Ref. [15]. The functions $f_{\pm}(k)$ in (5) characterize the crossed interaction (1) between unpaired fermions and BE-condensed CPs with $K = 0$; they are really the Fourier transforms of the internal bound-state wavefunction of the *extended* composite bosonic CPs. If $f_{\pm}(\varepsilon)$ are just the functions $f_{\pm}(k)$ with $k = \sqrt{2m\varepsilon}/\hbar$, we shall assume the steplike symmetric forms

$$f_{\pm}(\varepsilon) = \begin{cases} f & \text{for } \frac{1}{2}[E_{\pm}(0) - \delta\varepsilon] < \varepsilon < \frac{1}{2}[E_{\pm}(0) + \delta\varepsilon] , \\ 0 & \text{otherwise} , \end{cases} \quad (6)$$

where f is a positive coupling constant that along with CP energies $E_{\pm}(0)$ may be taken as the *phenomenological* parameters of the CBFM for arbitrary eh CP symmetry. Since $E_{\pm}(0)$ are the 2e- and 2h-CP energies for $\mathbf{K} = 0$, if $E_+(0) > E_-(0)$ we may define the positive parameter

$$\delta\varepsilon \equiv \frac{1}{2}[E_+(0) - E_-(0)] , \quad (7)$$

entering (6), so that the step-functions $f_{\pm}(\varepsilon)$ are *contiguous* to each other in energy. The case of *overlapping* step-functions, to be addressed elsewhere, is also interesting as it generates a “pseudogap”. This gap emerges *above* the regular critical temperature T_c but below a “depairing” temperature T^* a few times larger than T_c . Several recent experiments (see, e.g., Ref. [38, and references therein]) suggest the pseudogap and the ordinary superconducting gap to be merely different aspects of the same phenomena.

We now define a phenomenological *energy scale*

$$E_f \equiv \frac{1}{4}[E_+(0) + E_-(0)] , \quad (8)$$

not to be confused with the usual Fermi energy of an IFG

$$E_F \equiv \hbar^2 k_F^2 / 2m = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}, \tag{9}$$

in 3D, where k_F is the Fermi wavenumber of the IFG of electrons, with fermion-number density $n \equiv N/L^3 = k_F^3 / 3\pi^2$ and L^3 the system volume. Both E_f and E_F coincide *only* for perfect eh CP symmetry. The three parameters f , E_f and $\delta\varepsilon$ now become the main phenomenological parameters of the CBFM. With (7) and (8) one has

$$E_{\pm}(0) = 2E_f \pm \delta\varepsilon. \tag{10}$$

In contrast to BCS-B theory, in the CBFM the energies $E_{\pm}(0)$ of “nonmoving” (i.e., $\mathbf{K}=0$) CPs are not straightforwardly associated with the Fermi energy E_F , nor with the total fermion-number density n of the IFG ground state to which the interacting ground state goes continuously in the limit of vanishing interaction. In the present generalized theory which the CBFM in effect is, the parameters $E_{\pm}(0)$ are completely independent from the parameter E_F which is determined by the total electron density n .

The dynamical operator (5) can be diagonalized exactly via the so-called Bogoliubov–Valatin [39] transformation. The corresponding thermodynamic (or grand) potential $\Omega \equiv -PL^3$ for the BF mixture with P its pressure, is

$$\Omega(T, L^3, \mu, N_0, M_0) = -k_B T \ln[\text{Tr} e^{-\beta(\hat{H} - \mu\hat{N})}], \tag{11}$$

where T is the absolute temperature, $\beta \equiv 1/k_B T$, k_B the Boltzmann constant, μ the fermionic chemical potential, and “Tr” stands for “trace”. (Note: in Ref. [15] Ω was misnamed the Helmholtz free energy F , without affecting any results.) Using (5) in (11) we obtain

$$\begin{aligned} & \Omega(T, L^3, \mu, N_0, M_0) / L^3 \\ &= \int_0^\infty d\varepsilon N(\varepsilon) [\varepsilon - \mu - E(\varepsilon)] - 2k_B T \int_0^\infty d\varepsilon N(\varepsilon) \ln\{1 + \exp[-\beta E(\varepsilon)]\} \\ &+ [E_+(0) - 2\mu] n_0 + k_B T \int_0^\infty d\eta M(\eta) \ln\{1 - \exp[-\beta \mathcal{E}_+(\eta)]\} \\ &+ [2\mu - E_-(0)] m_0 + k_B T \int_0^\infty d\eta M(\eta) \ln\{1 - \exp[-\beta \mathcal{E}_-(\eta)]\}, \end{aligned} \tag{12}$$

where

$$N(\varepsilon) \equiv \frac{m^{3/2}}{2^{1/2} \pi^2 \hbar^3} \sqrt{\varepsilon}, \quad M(\eta) \equiv \frac{2m^{3/2}}{\pi^2 \hbar^3} \sqrt{\eta} \tag{13}$$

are the (one-spin) fermion and boson density of states at energies $\varepsilon = \hbar^2 k^2 / 2m$ and $\eta = \hbar^2 K^2 / 4m$, respectively. Also, the 2e- and 2h-boson energies $\mathcal{E}_+(\eta)$ and $\mathcal{E}_-(\eta)$ are defined through

$$\begin{aligned} E_+(K) - 2\mu &= \eta + E_+(0) - 2\mu \equiv \mathcal{E}_+(\eta), \\ 2\mu + E_-(K) &= \eta + 2\mu - E_-(0) \equiv \mathcal{E}_-(\eta). \end{aligned} \tag{14}$$

The fermion energy spectrum $E(\varepsilon)$ is gapped by an amount $\Delta(\varepsilon)$, i.e.,

$$E(\varepsilon) = \sqrt{(\varepsilon - \mu)^2 + \Delta^2(\varepsilon)}, \quad (15)$$

$$\Delta(\varepsilon) \equiv \sqrt{n_0} f_+(\varepsilon) + \sqrt{m_0} f_-(\varepsilon). \quad (16)$$

This last expression for the gap $\Delta(\varepsilon)$ implies a very simple T -dependence rooted in the two-electron n_0 and two-hole m_0 number densities of BE-condensed bosons, namely, $\Delta(T) = \sqrt{n_0(T)} f_+(\varepsilon) + \sqrt{m_0(T)} f_-(\varepsilon)$.

Minimizing $\Omega(T, L^3, \mu, N_0, M_0)$ with respect to N_0 and M_0 , and simultaneously fixing the total number N of electrons instead of its chemical potential μ , an equilibrium state of the system with volume L^3 and temperature T was characterized [15] by requiring that

$$\frac{\partial \Omega}{\partial N_0} = 0, \quad \frac{\partial \Omega}{\partial M_0} = 0, \quad \text{as well as} \quad \frac{\partial \Omega}{\partial \mu} = -N, \quad (17)$$

where N includes paired as well as unpaired fermions. After some algebra the *three coupled transcendental equations* (7)–(9) of Ref. [15] that determine n_0 and m_0 as well as μ , all as functions of temperature T and total electron density $n \equiv N/L^3$, followed. Simultaneous solution of those equations yields the thermodynamic functions

$$n_0 = n_0(T, \mu, n), \quad m_0 = m_0(T, \mu, n), \quad \mu = \mu(T, n). \quad (18)$$

Note that in Ref. [15] numerical calculations dealt *only* with the very special cases when either $n_0 = m_0$ (perfect eh CP symmetry) or when $m_0 = 0$ (no 2h-CPs present).

The pressure P , entropy S and specific heat at constant volume C of an equilibrium state characterized by T and n are then given by

$$P(T, n) = -\Omega/L^3, \quad S(T, n)/L^3 = -k_B \frac{\partial}{\partial T} (\Omega/L^3), \quad (19)$$

$$C(T, n)/L^3 = T \frac{\partial}{\partial T} [S(T, n)/L^3], \quad (20)$$

all evaluated at fixed $n_0(T, \mu, n)$, $m_0(T, \mu, n)$ and $\mu(T, n)$. The Helmholtz free energy $F(T, L^3, N) \equiv \Omega + \mu N$ then follows from

$$F(T, n)/L^3 = -P(T, n) + n \mu(T, n) \quad (21)$$

and the critical magnetic field is

$$\begin{aligned} H_c^2(T, n)/8\pi &\equiv F_n(T, n)/L^3 - F_s(T, n)/L^3 \\ &= P_s(T, n) - P_n(T, n) + [\mu_n(T, n) - \mu_s(T, n)]n \end{aligned} \quad (22)$$

with subindices s and n meaning “superconducting” and “normal” states.

3. BCS-B theory

As shown in Ref. [15] the equation for the fermionic energy gap $\Delta(\varepsilon)$, or $\Delta(T)$, of BCS-B theory—which has heretofore been strenuously proffered [40] as *not* being a BEC theory—follows from the CBFM for perfect eh CP symmetry and for a *specific* value of chemical potential, namely $\mu = E_f \simeq E_F$. In this section we recall how the BCS-B *energy gap equation* follows exactly from the new theory, and in the Appendix we show that the so-called “*condensation energy*” in the CBFM coincides with the familiar BCS-B expression in the weak-coupling limit. These two results, together with a later result dealing with dimensionless universal ratios, will completely justify the new statistical CBFM as a *generalized BCS-B* theory of superconductivity—which also reduces to several other theories as mentioned in the Introduction above.

Eqs. (7) and (8) of Ref. [15] were shown to coincide if $n_0(T) = m_0(T)$ (perfect eh CP symmetry), and to yield the gap equation of BCS-B theory provided that we set

$$\mu = E_f \equiv \frac{1}{4}[E_+(0) + E_-(0)] . \tag{23}$$

Besides, let

$$N(\varepsilon) = N(\mu) \quad \text{for } \mu - \delta\varepsilon < \varepsilon < \mu + \delta\varepsilon , \tag{24}$$

provided that $\delta\varepsilon \ll \mu$, which allows the true electron density of states $N(\varepsilon)$ in (12) to be replaced by the constant $N(\mu)$ in the narrow energy interval about μ . This introduces a convenient symmetry between electron- and hole-CPs in the vicinity of $\varepsilon = \mu$. From (10) and (23) we have

$$E_+(0) - 2\mu = 2\mu - E_-(0) = \delta\varepsilon . \tag{25}$$

Now (6) and (16) yield

$$\Delta(\varepsilon) = \begin{cases} \sqrt{n_0}f & \text{for } \mu < \varepsilon < \mu + \delta\varepsilon , \\ \sqrt{m_0}f & \text{for } \mu - \delta\varepsilon < \varepsilon < \mu , \\ 0 & \text{otherwise .} \end{cases} \tag{26}$$

Consequently, the 2e- and 2h-CP boson energies in (14) are really identical, namely

$$\mathcal{E}_+(\eta) = \mathcal{E}_-(\eta) = \eta + \delta\varepsilon . \tag{27}$$

If $m_0 = n_0$ (perfect eh CP symmetry) and in view of (23), Eqs. (7) and (8) of Ref. [15] coincide and on introducing $\xi \equiv \varepsilon - \mu$ become the gap equation of ordinary BCS-B theory. Also, since $m_0 = n_0$ the first two terms of (9) of Ref. [15] cancel and since $\mathcal{E}_+(\eta) = \mathcal{E}_-(\eta)$ so do the last two terms on the lhs as they are contributions from both 2e- and 2h-CPs with $K \neq 0$, so that (9) in Ref. [15] reduces to (15) there. For weak coupling one may further neglect Δ as a small correction, and restoring the full electron density of states $N(\varepsilon)$ in (15) of Ref. [15] yields the exact IFG relation (9) so that one may put $\mu = E_F$ as assumed in BCS-B theory. Then we can simply replace (15) in Ref. [15] by (9). Eq. (14) of Ref. [15] then becomes the fundamental BCS-B

energy gap equation (3.27) in Ref. [4], if we define

$$\frac{f^2}{2\delta\varepsilon} \equiv V, \quad \delta\varepsilon \equiv \hbar\omega_D, \quad (28)$$

where V is the BCS model interaction strength and ω_D is the Debye frequency. The gap equation was obtained in the original BCS theory from a physically inspired variational trial many-electron wave function. We see here that it is, in fact, the equation for *thermodynamic phase equilibria* in the BF system, *or*, the equation for determining the equilibrium number densities $n_0(T) = m_0(T)$ of BE-condensed bosons for perfect eh CP symmetry, since now from (6), (16) and (26)

$$\Delta(T) = f\sqrt{n_0(T)} = f\sqrt{m_0(T)}. \quad (29)$$

This relation is evidently *what links ordinary BCS-B and BEC theories*. Their critical temperature T_c will thus be the *same* since in BCS-B theory it is the temperature below which the fermionic gap opens, while in BEC it is that below which a Bose condensate appears.

The fundamental equation for the energy gap at $T=0$ is then easily integrated exactly to give

$$\Delta(0) \equiv \Delta = \frac{\delta\varepsilon}{\sinh(1/\lambda)} \xrightarrow{\lambda \rightarrow 0} 2\delta\varepsilon \exp(-1/\lambda), \quad (30)$$

where the dimensionless coupling parameter λ is

$$\lambda \equiv \frac{f^2 N(E_F)}{2\delta\varepsilon} \quad (31)$$

and where the last term in (30) is the weak-coupling limit. This is the familiar BCS-B theory result if as before we put $\delta\varepsilon = \hbar\omega_D$ and $\lambda = VN(E_F)$.

4. Phase diagram of the CBFM

In numerical calculations we refer fermion energies and chemical potential to the phenomenological energy E_f defined in (8), and use this as the unit of all energies. For temperatures we use the unit $T_f \equiv E_f/k_B$. For both condensate densities we used the unit $n_{f0} = m_{f0} \equiv E_f^2/f^2$, but for the total electron density n it is convenient to use another unit $n_f = (2mE_f)^{3/2}/3\pi^2\hbar^3$. We define a dimensionless crossed-interaction strength G (between two unpaired electrons and each of the two kinds of zero- K CPs) and a dimensionless energy-shell halfwidth de , by

$$G \equiv f^2 m^{3/2} / 2^{5/2} \pi^2 \hbar^3 E_f^{1/2} \quad \text{and} \quad de \equiv \delta\varepsilon / E_f. \quad (32)$$

To qualitatively illustrate the consequences of the generalized theory we fix these two dynamical parameters at $G = 10^{-4}$ and $de = 10^{-3}$, which by (28), (31) and (32) imply BCS interaction-model parameters $\lambda = 1/5$ and $\hbar\omega_D/E_F = 10^{-3}$. For the constant volume specific heat we use the unit $C_f = k_B m^{3/2} E_f^{3/2} / \pi^2 \hbar^3$, and for pressure P and free energy

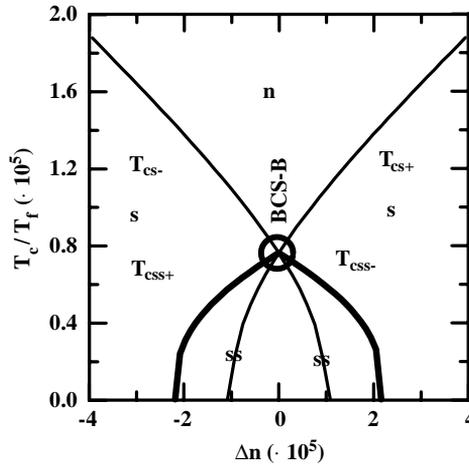


Fig. 1. Phase diagram with superconducting critical temperatures T_{cs+} , T_{cs-} , T_{css+} , and T_{css-} as defined in text, as functions of $\Delta n \equiv n/n_f - 1$ with n the total electron density and n_f defined just above (32), in the vicinity of the density $n = n_c \simeq n_f$ (see text) corresponding to BCS-B theory. Large circle contains intersection with value (34).

per unit volume F/L^3 the unit $P_f \equiv F_f/L^3 \equiv 2^{1/2}m^{3/2}E_f^{5/2}/\pi^2\hbar^3$. Finally, for the critical superconducting magnetic field H_c the unit $H_f \equiv m^{3/4}E_f^{5/4}/2^{1/4}\pi\hbar^{3/2}$ is employed.

The coupled equations (7)–(9) of Ref. [15] were obtained by minimizing Ω over condensate densities n_0, m_0 , and are valid at *internal* points ($n_0 > 0, m_0 > 0$) of the *full* physical domain $n_0 \geq 0, m_0 \geq 0$ defined by the quadrant with mutually perpendicular axes n_0 and m_0 . If parameters n and T are such that Ω is really a minimum, then at these values of n and T we have the solution for a true superconducting phase with a *mixed* condensate consisting of *both* kinds of zero- K CPs in varying proportions; we designate this phase by the symbol *ss*. However, the minimum of Ω might lie *on the boundary* of said quadrant, at: (a) $n_0 \neq 0, m_0 = 0$, or (b) $n_0 = 0, m_0 \neq 0$, or *the single point* (c) $n_0 = 0, m_0 = 0$. In such cases (7) and (8) of Ref. [15] become degenerate. In case (a) we omit (8) of Ref. [15] and put $m_0 = 0$ in (7) and (9) of Ref. [15]. In case (b) we omit (7) of Ref. [15] and put $n_0 = 0$ in (8) and (9) of Ref. [15]. In case (c) we need omit both (7) and (8) of Ref. [15] and put $n_0 = 0, m_0 = 0$ in (9) of Ref. [15]. These degenerate cases correspond to different equilibrium phases of the CBFM system. When at given (T, n) we have either case (a) or (b) we deal with solutions with a *pure-condensate* phase consisting of *either* 2e- or 2h-CPs; we designate these phases by the symbol *s*. Finally, when at given (T, n) case (c) holds, one has the *normal* phase solution with no condensate whatsoever; it is designated by the symbol *n*.

On the temperature/eh-CP-symmetry phase plane $(T, \Delta n)$ in the vicinity corresponding to BCS-B theory, numerical calculations suggest a complex diagram with four different possible equilibrium phases as illustrated in Fig. 1, where $\Delta n \equiv n/n_f - 1$ and

equals 0 for perfect eh CP symmetry where $T_f = T_F$. The curve labeled T_{cs+} ending on the abscissa at, say, Δn_{cs+} is the critical temperature of the 2e-CP-condensate phase s which lies below it. The curve T_{cs-} ending on the abscissa at Δn_{cs-} is the critical temperature of the 2h-CP-condensate phase s which lies below it. These curves intersect at $n = n_c$ (large circle in figure) and provide our *formal definition* of n_c . The region in the $(T, \Delta n)$ plane above both curves T_{cs+} and T_{cs-} corresponds to the *normal phase* consisting of an ideal BF gas. The region lying below the curves T_{css+} and T_{css-} and ending on the abscissa at, say, Δn_{css+} and Δn_{css-} corresponds to a *mixed-condensate phase* ss consisting of both 2e- and 2h-CPs. We find

$$\begin{aligned} \Delta n_c &= -0.467 \times 10^{-9}, \\ \Delta n_{cs+} &= -0.955 \times 10^{-5}, \quad \Delta n_{cs-} = 0.954 \times 10^{-5}, \\ \Delta n_{css+} &= -0.215 \times 10^{-4}, \quad \Delta n_{css-} = 0.215 \times 10^{-4}. \end{aligned} \quad (33)$$

Thus, for the relatively small values of G and de being used we neglect henceforth the difference between n_c and n_f as it is negligible for such weak two-fermion, crossed-interaction coupling, and simply put $n_c = n_f$. At the precise intersection (large circle in figure) where ordinary BCS-B theory applies, the critical temperature is the extremely small value

$$T_c^{BCS-B}/T_F = 7.64 \times 10^{-6} \quad (34)$$

though larger (and empirically more realistic) values are expected for larger values of G . This value is consistent with that obtained directly from the BCS T_c weak-coupling formula $k_B T_c \simeq 1.134 \hbar \omega_D \exp(-1/\lambda)$ for $\lambda = 1/5$.

A major result of this paper is that both 2e- ($s+$) or 2h-CP ($s-$) phase boundary curves *rise in temperature* as one departs from perfect eh symmetry and can yield substantially higher T_c 's than the mixed-condensate (ss) phase, for moderate departures from perfect eh CP symmetry. A second major result is that 2h-CP BEC T_c/T_F values are consistently higher (for equivalent departures from perfect eh CP symmetry) than 2e-CP ones, suggesting that “hole superconductors” in 3D have higher T_c/T_F values as observed [28,29]. This is because the factor T_f/T_F (needed to convert the phase boundary curves of Fig. 1 to refer to T_c/T_F instead of to T_c/T_f) is greater (less) than unity for $\Delta n \equiv n/n_f - 1 < (>) 0$.

In Fig. 2 the Helmholtz free energy F calculated numerically as function of T is shown for $\Delta n = 0$ (top) and $\Delta n = \pm 10^{-5}$ (bottom). Different phases are labelled as ss , s , n as explained before. For BCS-B theory ($\Delta n = 0$, top) as T is lowered below T_c^{BCS-B} the BCS-B ss phase separates out (or *bifurcates*) from the normal phase n , keeping below it as thermodynamically more stable. Besides this, at the same critical temperature T_c^{BCS-B} two additional coincident metastable phases s bifurcate from the normal phase n and lie between the ss and n phases. The BCS-B ss phase corresponds to a half-and-half mixture of condensed 2e- and 2h-CPs; an s phase has a pure condensate with 100% 2e-CPs or 100% 2h-CPs. So, in contrast to ordinary BCS-B the generalized theory gives not only the ss (stable) phase but also these two new *metastable* s phases, $s+$ and $s-$, with the same critical temperature T_c^{BCS-B} of

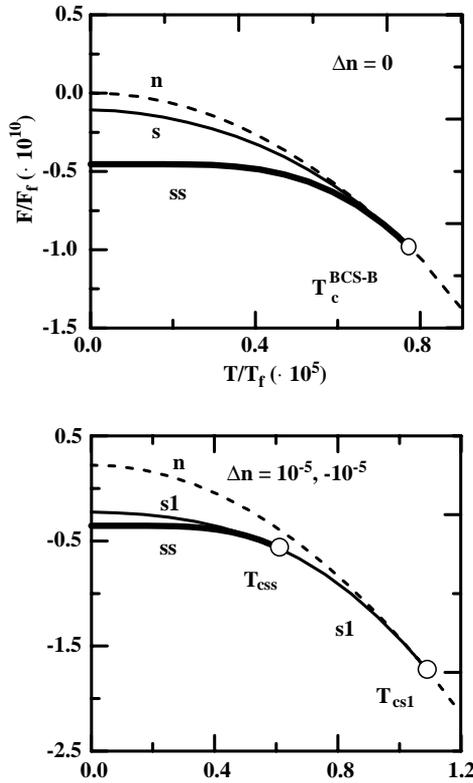


Fig. 2. Helmholtz free energy F as function of temperature T for $\Delta n \equiv n/n_f - 1 = 0$ (top) and for $\Delta n = \pm 10^{-5}$ (bottom). Open circles denote bifurcation points as discussed in text.

the BCS-B phase. In Fig. 2 (bottom) we also show how the phase picture changes as one changes Δn from 0 to $\pm 10^{-5}$ (with numerical calculations suggesting quite good symmetry of results at $\pm \Delta n$). We now have three critical temperatures T_{cs1} , T_{css} , and T_{cs2} (the latter not shown in figure). At the temperature T_{cs1} the superconducting phase $s1$ (with a pure condensate of 100% 2e-CPs when $n/n_f > 1$, or of 100% 2h-CPs when $n/n_f < 1$) bifurcates from the normal phase n . On lowering T another phase transition occurs, at critical temperature T_{css} , when the mixed ss phase (with condensate consisting of a roughly half-and-half mixture of condensed 2e- and 2h-CPs at $n/n_f \approx 1$) bifurcates from the phase $s1$. In the temperature range $T_{css} \leq T \leq T_{cs1}$ the true stable state is the phase $s1$, but it becomes metastable below T_{css} . At $T \leq T_{css}$ and down to $T = 0$ the stable state is the ss phase. A second (much more unstable) phase $s2$ (with its condensate, in contrast with the first phase $s1$, consisting either of 100% 2h-CPs with $n/n_c > 1$ or of 100% 2e-CPs when $n/n_c < 1$) bifurcates at some lower critical temperature $T_{cs2} < T_{css}$ from the normal n phase but is not shown in the figure.

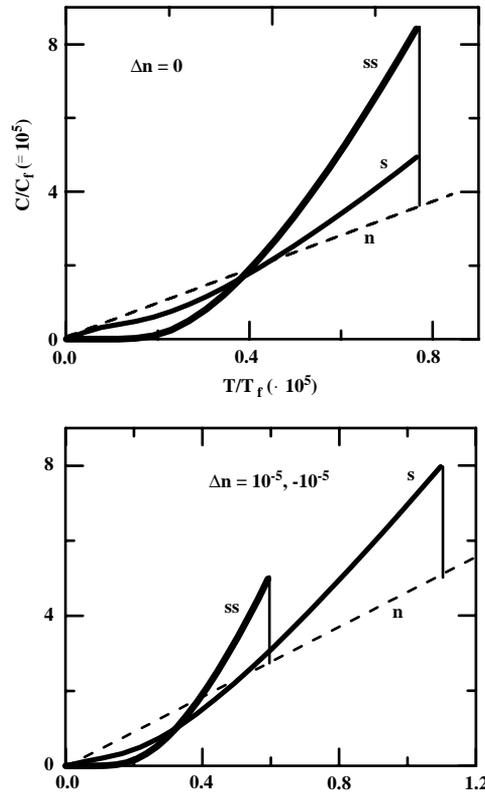


Fig. 3. Constant volume specific heat C as function of temperature T for $\Delta n = 0$ (top) and $\Delta n = \pm 10^{-5}$ (bottom).

Fig. 3 shows numerical curves for the constant volume specific heat C as function of T . At $\Delta n = 0$ when BCS-B theory is valid, both s and ss phases have the *same* critical temperature $T_{css}/T_F = T_{cs}/T_F = T_c^{BCS-B}/T_F$ given by (34), at which the specific heat suffers a jump discontinuity. If $C_n(T_c)$ is the normal phase specific heat at the critical temperature T_c , numerically we find the *dimensionless universal ratio* $\Delta C(T_c)/C_n(T_c) = 1.429$ for phase ss and 0.404 for phase s , which compares with the BCS-B result of $12/7\zeta(3) \simeq 1.43$, where $\zeta(3) \simeq 1.202$ is the Riemann Zeta function of order 3. The specific heat for the ss phase is larger than for the s phase just below T_c , but the opposite is true at lower temperatures. For $\Delta n = \pm 10^{-5}$ we have two critical temperatures $T_{cs}/T_f = 1.10 \times 10^{-5}$ and $T_{css}/T_f = 5.92 \times 10^{-6}$ and we find $\Delta C(T_c)/C_n(T_c) = 0.839$ for the ss phase and 0.587 for the s phase.

Numerically calculated curves for the free energy F , pressure P , entropy S , specific heat C and critical magnetic field H_c , each coincide at $\pm \Delta n$. So these quantities are (approximately) symmetric functions of Δn . Also, condensate densities satisfy the relation

$$n_0(\Delta n) = m_0(-\Delta n) \quad (35)$$

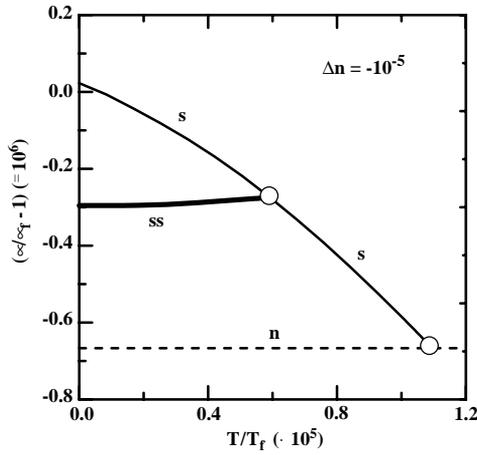


Fig. 4. Chemical potential μ as function of temperature T for $\Delta n = -10^{-5}$.

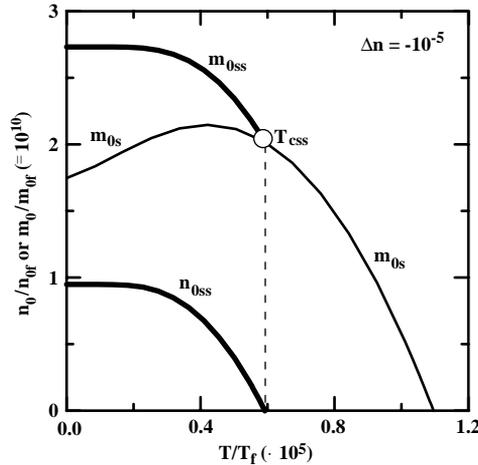


Fig. 5. Condensate densities n_0 and m_0 as function of temperature T for $\Delta n = -10^{-5}$, in units as explained in text.

for small Δn . However, the chemical potential $\mu/\mu_c - 1$ is an *antisymmetric* function of Δn , for small Δn . Here μ_c is the value of chemical potential at the point where all phase-boundary curves intersect each other (large circle in Fig. 1).

Figs. 4 and 5 illustrate numerical solution of Eqs. (7)–(9) of Ref. [15] at $\Delta n = -10^{-5}$. Chemical potentials μ as function of temperature T are shown in Fig. 4. The critical temperature for phase s is $T_{cs}/T_f = 1.10 \times 10^{-5}$ while for phase ss it is $T_{css}/T_f = 5.92 \times 10^{-6}$. In Fig. 5 are displayed condensate densities n_0 and m_0 of 2e-CPs and 2h-CPs, respectively, for phases s and ss . We see that for temperatures $T_{css} < T < T_{cs}$

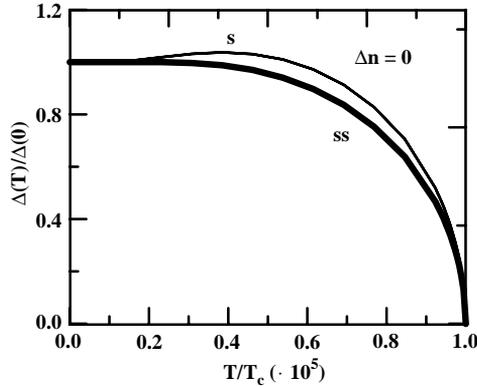


Fig. 6. Reduced fermionic energy gap $\Delta(T)/\Delta(0)$ as function of reduced temperature T/T_c for $\Delta n = 0$.

there exist *only* 2h-CPs ($m_0 = m_{0s}$), but at lower temperatures $0 < T < T_{css}$ the 2h-CPs phase s becomes metastable. In the region $0 < T < T_{css}$ there appears the mixed phase ss with condensate consisting of both 2e-CPs ($n_0 = n_{0ss}$) and 2h-CPs ($m_0 = m_{0ss}$), thick curves. Thus, above T_{css} the mixed 2e- and 2h-CPs-condensate disappears (in Fig. 5, $n_{0ss} = 0$) but the 2h-CPs-condensate survives (in Fig. 5, $m_{0ss} \neq 0$ at $T = T_{css}$). The mixed 2e- and 2h-CP condensate of the pure ss phase *evolves smoothly* into the pure 2h-CP condensate s phase.

In Fig. 6 are displayed numerically calculated curves for the reduced fermion energy gap $\Delta(T)/\Delta(0)$ as function of reduced temperature T/T_c for BCS-B theory, i.e., at $\Delta n = 0$, where $T_{css}/T_F = T_{cs}/T_F = T_c^{BCS-B}/T_F$ is given by (34). The thick curve marked ss numerically coincides with the BCS-B $\Delta(T)$ curve [41]. For the dimensionless gap-to- T_c universal ratio in the generalized theory we obtain $2\Delta(0)/k_B T_c = 3.528$ for phase ss and 2.385 for phase s , as compared with the ordinary BCS-B value of $2\pi/e^{\gamma} \simeq 3.528$ where $\gamma \simeq 0.57722$ is the Euler constant. At $\Delta n \neq 0$ we have in general *two* different fermionic energy gaps, according to (16), for phase ss , associated with electrons and holes, respectively. For phase s we have only one (either *electron* or *hole*) fermionic energy gap.

Lastly, Fig. 7 shows calculated curves for the critical magnetic field for both ss and s phases at $\Delta n = 0$, the dimensionless reduced critical magnetic field being defined by

$$h_c \left(\frac{T}{T_c} \right) \equiv \frac{H_c(T)}{H_c(0)} - \left[1 - \left(\frac{T}{T_c} \right)^2 \right]. \quad (36)$$

5. Conclusions

A complete (in the sense that two-hole Cooper pairs are not neglected) boson-fermion statistical model (CBFM) that constitute a generalized semi-phenomenological BCS-B microscopic theory of superconductivity leading to higher T_c 's was

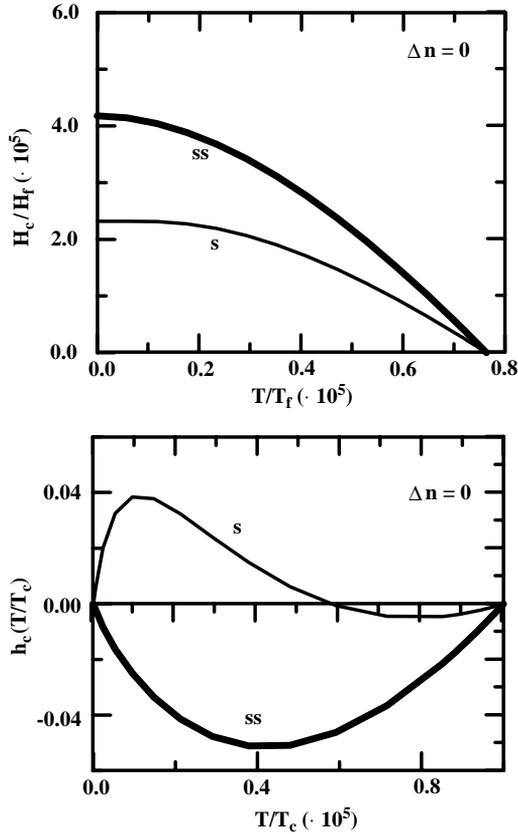


Fig. 7. Critical magnetic field (top) and reduced critical (bottom) magnetic field h_c (36) as functions of temperature T and reduced temperature T/T_c , respectively, for $\Delta n = 0$.

presented that contrasts with BCS-B theory in that besides temperature T there is a *second* crucial theoretical parameter describing arbitrary eh CP symmetry, namely $\Delta n \equiv n/n_f - 1 (\simeq n/n_c - 1)$ where $-1 < \Delta n < \infty$. This parameter is exactly zero for perfect eh CP symmetry as in BCS-B theory, where $n_c \simeq n_f$ is a certain critical value of n , the fermion-number density. Actually *tuning* a similar parameter in the normal state has become possible through very recent experiments [29] using the “field-effect transistor” technique of injecting holes in a material.

Ref. [15] showed that ordinary BCS-B theory holds in a very narrow region of density and weak unpaired-fermion/condensed-CP (two-fermion crossed) interaction for a BF mixture of pure 2e-CPs plus unpaired electrons. Such a weak coupling corresponds, e.g., to weak electron–phonon (four-fermion direct) coupling. In this paper we extracted BCS-B theory from the CBFM and showed it to be a BF system of 2e- and 2h-CPs (in a half-and-half proportion) plus unpaired electrons, for weak crossed interaction. In the CBFM the familiar BCS-B fermionic energy gap expression takes on definite

thermodynamic meaning as the equation of phase equilibrium of condensed CPs in a half-and-half CP mixture ($m_0 = n_0$) plus unpaired fermions.

As tedious numerical calculation shows, the detailed character of the differences between the CBFM and BCS-B theory depends on whether the interaction-strengths (6) overlap with each other or not, and also whether they have a rectangular form or not (as, e.g., a trapezoidal form). The case of overlapping step-functions admits an alternate explanation of the peculiar empirical behavior of the fermionic energy gap in some superconductors referred to as the “pseudogap”.

Finally and most importantly, it has been shown that in the CBFM both 2e- ($s+$) or 2h-CP ($s-$) phase boundary curves *rise* in temperature as one departs from perfect eh symmetry and can predict substantially higher T_c 's than BCS-B theory for moderate such departures. Although the CBFM reproduces all essential results of BCS-B theory for perfect eh symmetry in the asymptotic limit of weak interaction, it still appears to require additional *self-consistency conditions* linking the BCS-B theory zero- K CP energies $E_{\pm}(0)$ in (6) with the fermionic energy gap Δ , a matter that is beginning to be addressed elsewhere [33].

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Appendix A

To determine the *condensation energy* in the CBFM consider the ground-state energy. The Helmholtz free energy F of the equilibrium mixture system is

$$F \equiv E - TS = \Omega + \mu N, \quad (\text{A.1})$$

where Ω is the thermodynamic potential (11). At $T=0$ the free energy F gives exactly the ground-state energy E of the system. In the case of BCS-B theory $\mu_n = \mu_s = E_F$, and at $T=0$ from (12) with $n_0 = m_0$ the *condensation energy* per unit volume is

$$\frac{E_s - E_n}{L^3} = 2\delta\epsilon n_0 - 2N(E_F) \int_0^{\delta\epsilon} d\xi (\sqrt{\xi^2 + \Delta^2} - \xi), \quad (\text{A.2})$$

where $\xi \equiv \epsilon - E_F$ and (25) was used. Significantly, this is *different* from the original BCS theory expressions (2.41) and (2.43) of Ref. [4], namely

$$\frac{E_s - E_n}{L^3} = 2N(E_F) \int_0^{\hbar\omega_D} d\xi \left(\xi - \frac{\xi^2}{\xi^2 + \Delta^2} \right) - \frac{\Delta^2}{V} \xrightarrow{\lambda \rightarrow 0} -\frac{1}{2} N(E_F) \Delta^2, \quad (\text{A.3})$$

but in the limit $\lambda \rightarrow 0$ (A.2) gives precisely this BCS theory result, as we now show. The integral in (A.2) yields

$$\begin{aligned} & \frac{1}{2} \delta\epsilon \sqrt{\delta\epsilon^2 + \Delta^2} - \frac{\delta\epsilon^2}{2} - \frac{1}{2} \Delta^2 \ln \frac{\Delta}{\delta\epsilon + \sqrt{\delta\epsilon^2 + \Delta^2}} \\ &= -\frac{1}{2} \Delta^2 \ln \left(\frac{\Delta}{2\delta\epsilon} \right) + \frac{1}{4} \Delta^2 + o(\Delta^2). \end{aligned} \quad (\text{A.4})$$

Since from (29) $n_0 = \Delta^2/f^2$, Eq. (A.2) then becomes

$$\frac{E_s - E_n}{L^3} = -N(E_F) \Delta^2 \ln \left(\frac{\Delta}{2\delta\epsilon} \right) - \frac{1}{2} N(E_F) \Delta^2 + 2 \frac{\delta\epsilon}{f^2} \Delta^2 + o(\Delta^2). \quad (\text{A.5})$$

The first and the third terms on the rhs exactly cancel each other if (30) and (31) are used, and we finally obtain

$$\frac{E_s - E_n}{L^3} \xrightarrow{\lambda \rightarrow 0} -\frac{1}{2} N(E_F) \Delta^2, \quad (\text{A.6})$$

the familiar BCS theory result (A.3) if as before one identifies $\delta\epsilon = \hbar\omega_D$ and $\lambda = VN(E_F)$.

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