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A Generalized BEC Picture of Superconductors

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A recent re-examination of BCS theory leads one to devise a generalized BEC formalism (GBEC), that is, essentially a boson-fermion (BF) model containing three new ingredients: (i) Cooper pairs (CPs), in contrast to BCS pairs, as real bosons; (ii) BF vertex interactions (analogous to electron-phonon vertices); and (iii) two-hole CPs (2hCPs) accounted for along with two-electron CPs (2eCPs). In addition to the usual normal phase at high-enough temperatures T, three condensed phases emerge at lower temperatures with substantially higher T_cs than BCS theory. These are: two pure BEC phases of 2eCPs and of 2hCPs as well as a mixed phase with both kinds of CPs. BCS theory is precisely recovered with a mixed phase of equal numbers of both kinds of CPs. In contrast to the well-known BCS exponential rise from zero of T_c as function of carrier-number density the GBEC scheme exhibits the linear rise as function of doping as eminently observed in high-T_c underdoped superconductors such as YBCO. © 2012 Wiley Periodicals, Inc.

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Introduction

Boson-fermion (BF) models of superconductivity were apparently introduced by Ranninger and Robaszkiewicz as early as 1985,[1] Soon, a Bose-Einstein condensation (BEC) BF field theory by Friedberg and Lee and coworkers appeared.[2] Both these efforts, however, were binary BF models as they neglected, apparently for simplicity, the possibility of two-hole Cooper-pair (CP) bosons. Inclusion of 2h-CPs is essential to make precise contact with BCS theory possible. They lead to a generalized BEC (GBEC) formalism[3] describing a ternary BF model. This formalism relies on 2e-/2h-CP energies $E_{\pm}(K)$ phenomenologically, where K is the CP center-of-mass momentum (CMM) wavenumber. A (generalized) BEC (or macroscopic occupation of a given state that appears below a certain fixed $T = T_c$) was found[3] numerically *a posteriori* in the GBEC formalism. Two new phenomenological dynamical energy parameters $E_f \equiv \frac{1}{4}[E_+(0) + E_-(0)]$ and $\delta\varepsilon \equiv \frac{1}{2}[E_+(0) - E_-(0)] \geq 0$ can then be defined, where $E_{\pm}(0)$ are the (empirically unknown) zero-CMM energies of the 2e- and 2h-CPs, respectively. The E_f can be referred to as a 'pseudoFermi' energy, while $\delta\delta\varepsilon$ is usefully identified as the Debye energy $\hbar\omega_D$. The E_f merely serves as a convenient energy scale; it is not to be confused with the usual Fermi energy $E_F = \frac{1}{2}mv_F^2 \equiv k_B T_F$ where v_F and T_F are the Fermi velocity and Fermi temperature, respectively. If n is the total number density of charge-carrier electrons of effective mass m, the Fermi energy $E_F = (\hbar^2/2m)(3\pi^2 n)^{2/3}$ in 3D, whereas E_f is similarly related to another density n_f, which serves to scale the ordinary electron number density n. The two quantities E_f and E_F, and consequently also n and n_f, coincide only when perfect 2e/2h-CP symmetry holds as in the BCS instance.

Distinction Between Cooper and BCS Pairs

Whether the pairwise interfermion interaction is between charge carriers or between neutral atoms, a CP state of energy $E_{\pm}(K)$ will clearly be characterized only by a definite center-of-mass momentum wavevector $\mathbf{K} \equiv \mathbf{k_1} + \mathbf{k_2}$ but not definite relative momentum wavevector $\mathbf{k} \equiv \frac{1}{2}(\mathbf{k_1} - \mathbf{k_2})$. This is because, e.g., $E_+(K)$ itself is extracted from the Cooper eigenvalue equation

$$V\sum_{\mathbf{k}}{}' \left[\hbar^2 k^2/m + \hbar^2 K^2/4m - 2E_F - E_+(K)\right]^{-1} = 1 \qquad (1)$$

which involves a sum over $\mathbf{k}$. Although deceptively simple, this is elementary but a crucial point in all that follows.

The concept of a "Cooper pair" contrasts with that of a "BCS pair" defined[4] as a dimer with fixed $\mathbf{K}$ and $\mathbf{k}$ (or equivalently fixed $\mathbf{k}_1$ and $\mathbf{k}_2$), even though only the case $K = 0$ is considered in Ref. [4]. The BCS annihilation b_k and creation $b_k^\dagger$ operators are not quite bosonic since they obey the relations, Ref. [4] Eqs. (2.11) to (2.13),

$$\left[b_{\mathbf{k}}, b_{\mathbf{k}'}^\dagger\right] = (1 - n_{-\mathbf{k}\downarrow} - n_{\mathbf{k}\uparrow})\delta_{\mathbf{k}\mathbf{k}'} \qquad (2)$$

$$\left[b_{\mathbf{k}}^\dagger, b_{\mathbf{k}'}^\dagger\right] = [b_{\mathbf{k}}, b_{\mathbf{k}'}] = 0 \qquad (3)$$

where $n_{\pm\mathbf{k}s} \equiv a_{\pm\mathbf{k}s}^\dagger a_{\pm\mathbf{k}s}$ are fermion number operators, with creation $a_{\mathbf{k},s}^\dagger$ and annihilation $a_{\mathbf{k},s}$ operators referring to the fermions, and

$$\{b_{\mathbf{k}}, b_{\mathbf{k}'}\} = 2b_{\mathbf{k}}b_{\mathbf{k}'}(1 - \delta_{\mathbf{k}\mathbf{k}'}) \qquad (4)$$

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which is not quite fermionic, unless $\mathbf{k} = \mathbf{k}'$ when (2) is not bosonic. The precise Bose commutation relations are the familiar expressions

$$\left[b_{\mathbf{k}}, b^{\dagger}_{\mathbf{k}'}\right] = \delta_{\mathbf{k}\mathbf{k}'} \tag{5}$$

$$\left[b^{\dagger}_{\mathbf{k}}, b^{\dagger}_{\mathbf{k}'}\right] = [b_{\mathbf{k}}, b_{\mathbf{k}'}] = 0 \tag{6}$$

with (5) differing sharply from (2), at least formally. In contrast, the fermion creation $a^{\dagger}_{\mathbf{k}_1 s}$ and annihilation $a_{\mathbf{k}_1 s}$ operators satisfy the usual Fermi anti-commutation relations

$$\left\{a^{\dagger}_{\mathbf{k}_1 s}, a^{\dagger}_{\mathbf{k}'_1 s'}\right\} = \left\{a_{\mathbf{k}_1 s}, a_{\mathbf{k}'_1 s'}\right\} = 0 \tag{7}$$

$$\left\{a_{\mathbf{k}_1 s}, a^{\dagger}_{\mathbf{k}'_1 s'}\right\} = \delta_{\mathbf{k}_1 \mathbf{k}'_1}\delta_{ss'}. \tag{8}$$

The distinction between BCS pairs and CPs holds for the original or "ordinary" CPs.[5] It also applies to the generalized[6] (and including many-body effects) Bethe-Salpeter CPs defined more consistently without excluding two-hole pairs when the lower limit in the BCS interaction is taken as $\sqrt{k_F^2 - k_D^2}$ as in BCS theory,[4] where k_D is defined via the Debye energy $\hbar\omega_D \equiv \hbar^2 k_D^2/2m$.

The BCS-pair annihilation and creation operators for any $K \geq 0$ can be defined quite generally as

$$b_{\mathbf{k}\mathbf{K}} \equiv a_{\mathbf{k}_2\downarrow} a_{\mathbf{k}_1\uparrow} \quad \text{and} \quad b^{\dagger}_{\mathbf{k}\mathbf{K}} \equiv a^{\dagger}_{\mathbf{k}_1\uparrow} a^{\dagger}_{\mathbf{k}_2\downarrow} \tag{9}$$

where $a^{\dagger}_{\mathbf{k}_1 s}$ and $a_{\mathbf{k}_1 s}$ obey (7) and (8), and as before $\mathbf{k} \equiv \frac{1}{2}(\mathbf{k}_1 - \mathbf{k}_2)$ and $\mathbf{K} \equiv \mathbf{k}_1 + \mathbf{k}_2$ are the relative and CMM wavevectors, respectively, associated with two fermions with wavevectors

$$\mathbf{k}_1 = \mathbf{K}/2 + \mathbf{k} \quad \text{and} \quad \mathbf{k}_2 = \mathbf{K}/2 - \mathbf{k}. \tag{10}$$

Using the same techniques to derive (2) to (4) valid for $K = 0$, the operators $b_{\mathbf{k}\mathbf{K}}$ and $b^{\dagger}_{\mathbf{k}\mathbf{K}}$ are found[7] to satisfy: (a) the "pseudo-boson" commutation relations

$$\left[b_{\mathbf{k}\mathbf{K}}, b^{\dagger}_{\mathbf{k}'\mathbf{K}}\right] = (1 - n_{\mathbf{K}/2-\mathbf{k}\downarrow} - n_{\mathbf{K}/2+\mathbf{k}\uparrow})\delta_{\mathbf{k}\mathbf{k}'} \tag{11}$$

$$\left[b^{\dagger}_{\mathbf{k}\mathbf{K}}, b^{\dagger}_{\mathbf{k}'\mathbf{K}}\right] = [b_{\mathbf{k}\mathbf{K}}, b_{\mathbf{k}'\mathbf{K}}] = 0 \tag{12}$$

where $n_{\mathbf{K}/2\pm\mathbf{k}s} \equiv a^{\dagger}_{\mathbf{K}/2\pm\mathbf{k}s} a_{\mathbf{K}/2\pm\mathbf{k}s}$ are fermion number operators; as well as (b) a "pseudo-fermion" anti-commutation relation

$$\{b_{\mathbf{k}\mathbf{K}}, b_{\mathbf{k}'\mathbf{K}}\} = 2b_{\mathbf{k}\mathbf{K}} b_{\mathbf{k}'\mathbf{K}}(1 - \delta_{\mathbf{k}\mathbf{k}'}). \tag{13}$$

Our only restriction was that $\mathbf{K} \equiv \mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}'_1 + \mathbf{k}'_2$. If $K = 0$ so that $\mathbf{k}_1 = -\mathbf{k}_2 = \mathbf{k}$ (the only case considered by BCS), and calling $b_{\mathbf{k}\mathbf{K}=\mathbf{0}} \equiv b_{\mathbf{k}}$, etc., (11) to (13) become (2) to (4), as they should. So, neither BCS pairs with $K = 0$ 0 are bosons as the relation (11) contains additional terms not[8] present in the usual boson commutation relations analogous to (5).

To our knowledge, no one has yet succeeded in constructing CP creation and annihilation operators that obey Bose commutation relations, starting from fermion creation $a^{\dagger}_{\mathbf{k}_1 s}$ and annihilation $a_{\mathbf{k}_1 s}$ operators, as is postulated in Refs. [9,10] in a generalized BEC theory that contains BCS theory as a special case. This postulation is grounded in magnetic-flux quantization experiments[11–13] that establish the presence of charged pairs—albeit without being able (Gough, personal communication) to specify the sign of those charges. However, although the eigenvalues of $b^{\dagger}_{\mathbf{k}\mathbf{K}} b_{\mathbf{k}\mathbf{K}}$ are 0 or 1 in keeping with the Pauli Exclusion Principle, those of $\sum_{\mathbf{k}} b^{\dagger}_{\mathbf{k}\mathbf{K}} b_{\mathbf{k}\mathbf{K}}$ are evidently $0, 1, 2\cdots$ because of the indefinitely many values taken on by the summation index $\mathbf{k}$. This implies BE statistics and corroborates the qualitative conclusions reached above. A discussion in greater detail of this is found in Refs. [14,15].

Generalized BEC Formalism (GBEC)

The GBEC formalism is described in detail in Refs. [9,10]; here we summarize its main equations. It applies in d dimensions and is defined by a Hamiltonian of the form $H = H_0 + H_{\text{int}}$. The unperturbed Hamiltonian H_0 should ideally be, to quote Leggett[16] "an appropriate (zeroth-oder) starting point" accounting for "pairs of electronic excitations with charge 2e that all have the same ground-state wavefunction." Thus, our H_0 corresponds to a non-Fermi-liquid "normal" state which, besides just fermions, is an ideal (i.e., noninteracting) ternary gas mixture of unpaired fermions and both types of CPs namely, 2e and 2h, the latter introduced without loss of generality. Specifically

$$H_0 = \sum_{\mathbf{k}_1, s_1} \epsilon_{\mathbf{k}_1} a^{+}_{\mathbf{k}_1, s_1} a_{\mathbf{k}_1, s_1} + \sum_{\mathbf{K}} E_{+}(K) b^{+}_{\mathbf{K}} b_{\mathbf{K}} - \sum_{\mathbf{K}} E_{-}(K) c^{+}_{\mathbf{K}} c_{\mathbf{K}} \tag{14}$$

where $\mathbf{K}$ is the previously defined CMM wavevector of the pair, while $\epsilon_{\mathbf{k}_1} \equiv \hbar^2 k_1^2/2m$ are the single-electron, and $E_{\pm}(K)$ the 2e-/2h-CP phenomenological, energies. Here $a^{+}_{\mathbf{k}_1, s_1}$ ($a_{\mathbf{k}_1, s_1}$) 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. These b and c operators depend only on $\mathbf{K}$ and so are distinct from the BCS operators depending on both $\mathbf{K}$ and the relative $\mathbf{k} \equiv \frac{1}{2}(\mathbf{k_1} - \mathbf{k_2})$ discussed in Ref. [4] Eqs. (2.9)–(2.13) for the particular case of $K = 0$ and shown there not to satisfy the ordinary Bose commutation relations. But because two pairs cannot exactly overlap in real space without violating the Pauli Principle, they are often considered "hard-core bosons," albeit of hard-core radii 0^{+}. For this reason, one can probably not expect to be able to construct the b and c operators directly from the a operators to establish that b and c obey Bose commutation relations precisely. Nonetheless, these pairs stand for objects that can easily be seen to obey Bose-Einstein statistics as, in the thermodynamic limit, an indefinitely large number of $\mathbf{k}$ values correspond to a given $\mathbf{K}$ value defining an energy level $E_{+}(K)$ or $E_{-}(K)$. This is all that is needed to ensure the BEC (or macroscopic occupation of a given state that appears below a certain fixed $T = T_c$) found[9,10] numerically *a posteriori* in the GBEC theory.

Furthermore, being noninteracting (except for the Pauli Principle restriction mentioned), CPs satisfy the Ehrenfest-Oppenheimer[17] criteria for two clusters of charges to conserve a specific kind of statistics, either Bose or Fermi. These assumed properties are justified *a posteriori* when in the GBEC theory: (a) the BCS gap equation is recovered for equal numbers of both kinds of pairs, both in the $K = 0$ state and in all $K \neq 0$ states taken collectively, and in weak coupling, regardless[18] of CP overlaps; and (b) the precise familiar BEC T_c formula emerges[9] when (i) 2h-CPs are ignored, the Friedberg–Lee model[19,20] equations are recovered and (ii) one switches off the BF interaction. The only difference in the recovered BEC T_c formula is that the boson number density now depends on T_c, as expected in a BF gas mixture where boson populations are T-dependent. Finally, we note that fermion scattering terms[21] are not included in (14) as they are not expected to be substantial, say, in the BCS limit of high electron density where they would be the most effective, which in turn is included in the GBEC model as a special case.

The interaction Hamiltonian $H_{\rm int}$ in the expression $H = H_0 + H_{\rm int}$ describes the formation and disintegration of CPs, respectively, from and into unpaired electrons and unpaired holes. It is further simplified by dropping all $K \neq 0$ terms. This is also done in BCS theory in its full} Hamiltonian $H = H_0 + H_{\rm int}$, but kept in the GBEC theory in its unperturbed H_0 portion (14). The GBEC $H_{\rm int}$ is made up of four distinct BF interaction vertices each with two-fermion/one-boson creation and/or annihilation operators. These vertices depict how unpaired electrons (subindex $+$) [or holes (subindex $-$)] are involved in the formation and disintegration of the 2e- (and 2h-) $K = 0$ CPs in the d-dimensional system of size L, namely.

$$H_{\rm int} = L^{-d/2}\sum_{\mathbf{k}} f_+(k)\{a^+_{\mathbf{k},\uparrow}a^+_{-\mathbf{k},\downarrow}b_{\mathbf{0}} + a_{-\mathbf{k},\downarrow}a_{\mathbf{k},\uparrow}b^+_{\mathbf{0}}\} + L^{-d/2}\sum_{\mathbf{k}} f_-(k)\{a^+_{\mathbf{k},\uparrow}a^+_{-\mathbf{k},\downarrow}c^+_{\mathbf{0}} + a_{-\mathbf{k},\downarrow}a_{\mathbf{k},\uparrow}c_{\mathbf{0}}\} \tag{15}$$

where $\mathbf{k} \equiv \frac{1}{2}(\mathbf{k_1} - \mathbf{k_2})$ as before is the relative momentum wavevector of a CP. The interaction vertex form factors $f_\pm(k)$ in (15) are essentially the Fourier transforms of the 2e- and 2h-CP intrinsic wavefunctions, respectively, in the relative coordinate of the two fermions. The GBEC theory is thus reminiscent of the Sommerfeld theory of the electron gas combined with the Debye picture of the phonon gas which together give a binary mixture of noninteracting electrons and phonons, a picture which describes quite well low-T specific heats in metals and insulators. But to explain either resistance and superconductivity, they must then be allowed to interact via the Fröhlich electron-phonon interaction[22] of a form analogous to (15) but without hole terms.

The grand (sometimes called the Landau) thermodynamic potential Ω associated with the full Hamiltonian $H = H_0 + H_{\rm int}$ given by (14) and (15) is then constructed via (Ref. [23] Eq. 4.14) the definition

$$\Omega(T, L^{\rm d}, \mu, N_0, M_0) = -k_{\rm B}T\ln\left[{\rm Tr}e^{-\beta(H-\mu\hat{N})}\right] \tag{16}$$

where "Tr" stands for "trace" and $\beta \equiv 1/k_{\rm B}T$ with T the absolute temperature. It is related to the system pressure P, internal energy E and entropy S by $\Omega = -PL^{\rm d} = F - \mu N = E - TS - \mu N$, where F is the Helmholtz free energy.

Following the Bogoliubov prescription,[24] one sets b^+_0, b_0 equal to $\sqrt{N_0}$ and c^+_0, c_0 equal to $\sqrt{M_0}$ in (15), where N_0 is the T-dependent number of zero-CMM 2e-CPs and M_0 likewise for 2h-CPs. This allows exact diagonalization for any coupling, through a Bogoliubov transformation of the a^+, a fermion operators, giving after some algebra

$$\begin{aligned}\Omega(T, L^{\rm d}, \mu, N_0, M_0)/L^{\rm d} = &\int_0^\infty d\epsilon N(\epsilon)[\epsilon - \mu - E(\epsilon)] - 2k_{\rm B}T\int_0^\infty d\epsilon N(\epsilon)\ln\{1 + \exp[-\beta E(\epsilon)]\}\\ &+ [E_+(0) - 2\mu]n_0 + k_{\rm B}T\int_0^\infty d\varepsilon M(\varepsilon)\ln\{1 - \exp[-\beta\{E_+(0) + \varepsilon - 2\mu\}]\}\\ &+ [2\mu - E(0)]m_0 + k_{\rm B}T\int_{0+}^\infty d\varepsilon M(\varepsilon)\ln\{1 - \exp[-\beta\{2\mu - E(0) + \varepsilon\}]\}.\end{aligned} \tag{17}$$

Here $N(\epsilon)$ and $M(\varepsilon)$ are respectively the electronic and bosonic density of states, while

$$E(\epsilon) \equiv \sqrt{(\epsilon - \mu)^2 + \Delta^2(\epsilon)} \equiv \sqrt{(\epsilon - \mu)^2 + n_0 f_+^2(\epsilon) + m_0 f_-^2(\epsilon)} \tag{18}$$

since $\Delta(\epsilon) = \sqrt{n_0}f_+(\epsilon) + \sqrt{m_0}f_-(\epsilon)$ where $f_+(\epsilon)$ and $f_-(\epsilon)$ can be constructed as in Ref. [9] as non-overlapping Heaviside functions so that $f_+(\epsilon)f_-(\epsilon) \equiv 0$, while $n_0(T) = N_0(T)/L^{\rm d}$ and $m_0(T) = M_0(T)/L^{\rm d}$ are the 2e-CP and 2h-CP number densities, respectively, of BE-condensed (i.e., with $K = 0$) bosons.

Minimizing F with respect to N_0 and M_0, while simultaneously fixing the total number N of electrons by introducing the electron chemical potential m in the usual way, namely

$$\frac{\partial F}{\partial N_0} = 0, \qquad \frac{\partial F}{\partial M_0} = 0, \qquad \text{and} \qquad \frac{\partial \Omega}{\partial \mu} = -N \tag{19}$$

ensures an equilibrium thermodynamic state of the system with volume $L^{\rm d}$ at temperature T and chemical potential μ. Evidently, N includes both paired and unpaired CP electrons. The following relies on the relation $E_{\rm f} \equiv \frac{1}{4}[E_+(0) + E_-(0)]$ mentioned above, which in turn implies that

$$E_\pm(0) = 2E_{\rm f} \pm \delta\varepsilon. \tag{20}$$

Some algebra then leads to the three coupled integral Eqs. (7)-(9) of Ref. [9] with $f_+(\epsilon)f_-(\epsilon) \equiv 0$. These expressions can be simplified to the two "gap-like equations"

$$[2E_{\rm f} + \delta\varepsilon - 2\mu(T)] = \frac{1}{2}f^2\int_{E_{\rm f}}^{E_{\rm f}+\delta\varepsilon} d\epsilon N(\epsilon)\frac{\tanh\frac{1}{2}\beta\sqrt{[\epsilon - \mu(T)]^2 + f^2 n_0(T)}}{\sqrt{[\epsilon - \mu(T)]^2 + f^2 n_0(T)}} \tag{21}$$

$$[2\mu(T) - 2E_f + \delta\varepsilon] = \frac{1}{2} f^2 \int_{E_f - \delta\varepsilon}^{E_f} d\epsilon N(\epsilon) \frac{\tanh \frac{1}{2}\beta\sqrt{[\epsilon - \mu(T)]^2 + f^2 m_0(T)}}{\sqrt{[\epsilon - \mu(T)]^2 + f^2 m_0(T)}} \tag{22}$$

and a single "number equation" (which guarantees charge conservation)

$$2n_B(T) - 2m_B(T) + n_f(T) = n. \tag{23}$$

where

$$n_f(T) \equiv \int_0^\infty d\epsilon N(\epsilon) \left[1 - \frac{\epsilon - \mu}{E(\epsilon)} \tanh \frac{1}{2}\beta E(\epsilon)\right]. \tag{24}$$

In (23) $n \equiv N/L^d$ is the number density of electrons while $n_B(T)$ and $m_B(T)$ are, respectively, the number densities of 2e- and 2h-CPs in all bosonic states (both $K = 0$ as well as $K > 0$). Evidently, $n_f(T)$ in (24) is evidently the number of unpaired electrons. The "complete" number equation (23) can be rewritten more explicitly as

$$2n_0(T) + 2n_{B+}(T) - 2m_0(T) - 2m_{B+}(T) + n_f(T) = n \tag{25}$$

where $n_B(T)$ is

$$\begin{aligned} &n_B(T) \equiv n_0(T) + n_{B+}(T) \quad \text{where} \\ &n_{B+}(T) \equiv \int_{0+}^{\infty} d\varepsilon M(\varepsilon)[\exp\beta\{E_+(0) + \varepsilon - 2\mu\} - 1]^{-1} \end{aligned} \tag{26}$$

and similarly for $m_B(T)$ which is

$$\begin{aligned} &m_B(T) \equiv m_0(T) + m_{B+}(T) \quad \text{where} \\ &m_{B+}(T) \equiv \int_{0+}^{\infty} d\varepsilon M(\varepsilon)[\exp\beta\{2\mu - E_-(0) + \varepsilon\} - 1]^{-1}. \end{aligned} \tag{27}$$

Clearly, $m_{B+}(T)$ are precisely the number of "pre-formed" $K > 0$ 2h-CPs, and $n_{B+}(T)$ that of 2e-CPs. These CPs are non-condensed in contrast with the $K = 0$ CPs which are BE condensed. Evaluating the integrals requires knowing the bosonic density-of-states $M(\varepsilon)$ of CPs of energy ε, which in turn requires knowing the dispersion relation ε vs. K. When the number densities of 2eCPs and 2hCPs are equal in both $K = 0$ and in all $K \neq 0$ states, one derives the central result that the original crossover picture for unknowns $\Delta(T)$ and $\mu(T)$ is now supplemented by the central relation

$$\Delta(T) = f\sqrt{n_0(T)} = f\sqrt{m_0(T)} \tag{28}$$

that links the order parameters of BCS and BEC theories quite simply.

All three order-parameter functions $\Delta(T), n_0(T)$ and $m_0(T)$ have the familiar "half-bell-shaped" forms. Namely, they are zero above a certain critical temperature T_c, and rise monotonically upon cooling (lowering T) to maximum values $\Delta(0)$, $n_0(0)$ and $m_0(0)$ at $T = 0$. The energy gap $\Delta(T)$ is the order parameter describing the superconducting (or superfluid) condensed state, while $n_0(T)$ and $m_0(T)$ are the BEC order parameters depicting the macroscopic occupation that occurs below T_c in a BE condensate.

This $\Delta(T)$ is precisely the BCS energy gap if the boson-fermion coupling f is made to correspond to $\sqrt{2V\hbar\omega_D}$ within the GBEC formalism. Evidently, the BCS and BEC T_c s are the same. Writing (28) for $T = 0$ and dividing this into (28) gives the much simpler f-independent relation involving order parameters normalized to unity in the interval $[0, 1]$, specifically

$$\begin{aligned} \Delta(T)/\Delta(0) &= \sqrt{n_0(T)/n_0(0)} \\ &= \sqrt{m_0(T)/m_0(0)} \underset{T\to 0}{\longrightarrow} 1 \\ &\underset{T\geq T_c}{\longrightarrow} 0. \end{aligned} \tag{29}$$

The first equality, apparently first obtained in Ref. [25], connects in a simple way the two heretofore unrelated "half-bell-shaped" order parameters of the BCS and the BEC theories. The second equality[9,10] implies that a BCS condensate is precisely a GBE condensate of equal numbers of 2e- and 2h-CPs. Since (29) is independent of the particular vertex dynamics of the problem, it can be expected to hold for either superconductors or fermionic superfluids such as ultracold fermionic atoms. Using (20) yields precisely the BCS gap equation for all T, Eq. (3.27) of Ref. [4], provided one picks $E_f = \mu$, namely

$$1 = \lambda \int_0^{\hbar\omega_D} d\xi \frac{1}{\sqrt{\xi^2 + \Delta^2(T)}} \tanh \frac{1}{2}\beta\sqrt{\xi^2 + \Delta^2(T)} \tag{30}$$

where $\xi \equiv \epsilon - \mu$, since $\lambda \equiv N(E_F)V = f^2 N(E_F)/2\delta\varepsilon$ while $n_B(T) = m_B(T)$ [see relation between V and f stated just above (28)], and provided $N(\varepsilon)$ can be taken outside the integral signs in (21) and (22). This last operation is exact in 2D when $N(\epsilon)$ is independent of $N(\epsilon)$ and is otherwise a good approximation if $\hbar\omega_D \ll \mu$ in 3D.

However, the choice $E_f = \mu$ cannot be justified, to our knowledge, without assuming within the GBEC that $n_B(T) = m_B(T)$ as well as $n_0(T) = m_0(T)$, i.e., by explicitly recognizing the existence of 2h-CPs along with 2e-CPs and taking them in equal or 50-50 proportions.

Condensation Energy

The $T = 0$ condensation energy per unit volume according to the GBEC theory, given (18), is

$$\frac{E_s - E_n}{L^d} = \frac{\Omega_s(T = 0) - \Omega_n(T = 0)}{L^d} \tag{31}$$

since for any T the Helmholtz free energy $F \equiv E - TS = \Omega + \mu N$, with S the entropy, and μ is the same for either superconducting s or normal n phases with internal energies E_s and E_n, respectively. In the normal phase $n_0(T) = 0$, $m_0(T) = 0$ so that $\Delta(T) = 0$ for all $T \geq 0$, so that (18) reduces to

$$\frac{\Omega_n(T=0)}{L^d} = \int_0^\infty d\epsilon N(\epsilon)(\epsilon - \mu - |\epsilon - \mu|) = 2\int_0^\mu d\epsilon N(\epsilon)(\epsilon - \mu) = 2\int_{-\mu}^0 d\xi N(\xi)\xi. \quad (32)$$

For the superconducting phase, and when $n_0(T) = m_0(T)$ and $n_B(T) = m_B(T)$ hold one deduces from (20) and (18) that $\mu = E_f$. Putting $\Delta(T=0) \equiv \Delta$ in (18) as well as $\delta\varepsilon \equiv \hbar\omega_D$, while using (20), gives

$$\frac{\Omega_s(T=0)}{L^d} = 2\hbar\omega_D n_0(0) + \int_{-\mu}^\infty d\xi N(\xi)\left(\xi - \sqrt{\xi^2+\Delta^2}\right) = 2\hbar\omega_D n_0(0) + 2\int_{-\mu}^{-\hbar\omega_D} d\xi N(\xi)\xi - 2\int_0^{\hbar\omega_D} \times d\xi N(\xi)\sqrt{\xi^2+\Delta^2}. \quad (33)$$

The first factor of 2 in the last line comes precisely from the condition $n_0(T) = m_0(T)$ while the last two factors of 2 arise from the condition that the magnitudes of $f_+(\epsilon)$ and $f_-(\epsilon)$ be the same and equal to, say, *f*.

Subtracting (32) from (33) and putting $N(\xi) \cong N(0)$, the density of electronic states at the Fermi surface [designated before as $N(E_F)$] yields

$$\frac{E_s - E_n}{L^d} = 2\hbar\omega_D n_0(0) + 2N(0)\int_0^{\hbar\omega_D} d\xi\left(\xi - \sqrt{\xi^2+\Delta^2}\right) = 2\hbar\omega_D n_0(0) + N(0)\left[(\hbar\omega_D)^2 - \hbar\omega_D\sqrt{(\hbar\omega_D)^2+\Delta^2} + \Delta^2 \ln\frac{\Delta}{\hbar\omega_D + \sqrt{(\hbar\omega_D)^2+\Delta^2}}\right] \quad (34)$$

exactly, by standard integrations. Using the expression that follows from (30) for $T = 0$ gives Eq. (2.40) of Ref. [4], namely

$$\Delta = \frac{\hbar\omega_D}{\sinh(1/\lambda)} \quad (35)$$

where λ is related to the GBEC BF interaction parameter *f* through

$$\lambda \equiv VN(0) = f^2 N(0)/2\hbar\omega_D. \quad (36)$$

This makes the first term on the rhs of (34) exactly equal to $\Delta^2 N(0)/\lambda$ which in turn can be shown to cancel exactly against the log term if one recalls the hyperbolic-function identity $\sinh^2 x + 1 \equiv \cosh^2 x$. Thus, the GBEC theory condensation energy (34) is identical for any coupling to that of BCS theory, Eq. (2.42) of Ref. [4], namely

$$\frac{E_s - E_n}{L^d} = N(0)(\hbar\omega_D)^2\left[1 - \sqrt{1+(\Delta/\hbar\omega_D)^2}\right] \underset{\lambda\to 0}{\to} -\frac{1}{2}N(0)\Delta^2\left[1 - \frac{1}{4}\left(\frac{\Delta}{\hbar\omega_D}\right)^2 + O\left(\frac{\Delta}{\hbar\omega_D}\right)^4\right]. \quad (37)$$

This energy, associated with the expectation value of the BCS trial wavefunction gives a rigorous upper bound to the exact ground-state energy of the BCS Hamiltonian. Empirically, for niobium (Nb, bcc, $T_c \simeq 9.3$K, critical magnetic field $H_c \simeq 160$ kA/m) the condensation energy to be compared with the BCS result (37) works out to be just 2×10^{-6} eV/atom.[26] The equivalence of (34) and (37) seems to suggest that, as in the GBEC theory, there are no pair-pair interactions in the BCS theory either, as is evident from Hamiltonians (14) and (15) as well as the well-known BCS Hamiltonian.

The octant depicted in Figure 1 illustrates the applicability at any temperature *T* and any electron concentration *n* of the

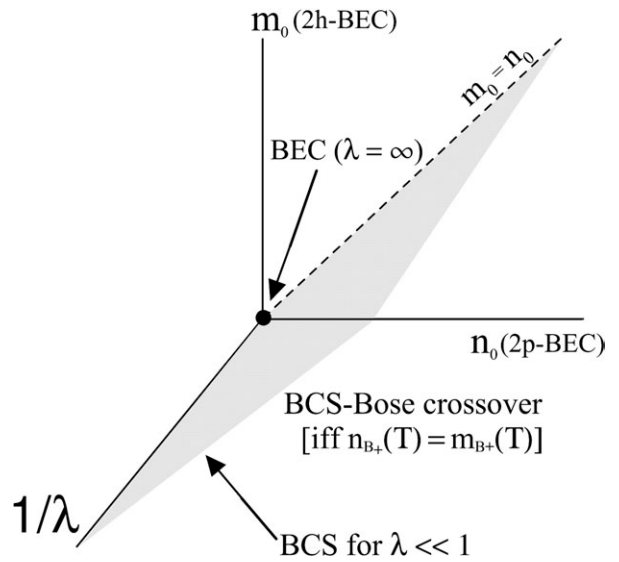

Figure 1. Parameter octant defined by the two condensate densities $n_0(T) \geq 0$ and $m_0(T) \geq 0$ as well as the (also non-negative) inverse $1/\lambda \geq 0$ of the interelectronic BCS dimensionless coupling $\lambda \geq 0$, and applicable in principle at all temperatures *T*. GBEC describes a ternary gas and applies in the entire octant. The BCS-Bose crossover theory applies only on the shaded plane defined by $n_0(T) \equiv m_0(T)$ provided the additional restriction $n_{B+}(T) = m_{B+}(T)$ is imposed whereby the total number of 2p (two-electron) noncondensate CPs equals that of 2h (two-hole) CPs. BCS theory is valid along the forefront of the shaded plane where $\lambda \ll 1$ of the shaded BCS-Bose crossover plane. For quadratically dispersive bosons the usual BEC theory ensues at the origin of the octant where $m_0(T) = 0$ for all *T* and $n_0(T_c) = 0$, giving there the implicit expression $T_c \simeq 3.31\hbar^2 n_B(T_c)^{2/3}/2mk_B$. This has the same form as the standard explicit BEC T_c -formula for mass 2m bosons and where the boson number density n_B is, of course, independent of T_c.

BCS-Bose crossover picture (shaded plane) and the BCS theory (forefront of said plane), both schemes with the familiar dimensionless coupling $\lambda \equiv N(E_F)V$ where *V* is the net attractive interelectronic interaction causing the formation of CPs. On the other hand, the applicability of the GBEC formalism spans the entire octant with vertical and horizontal axes defined by $m_0(T,n)$ and $n_0(T,n)$, respectively.

Results and Discussion

Numerical elimination of $\mu(T,n)$ has shown that, in addition to a normal phase defined by $n_0(T,n) = m_0(T,n) = 0$ at high *T*,

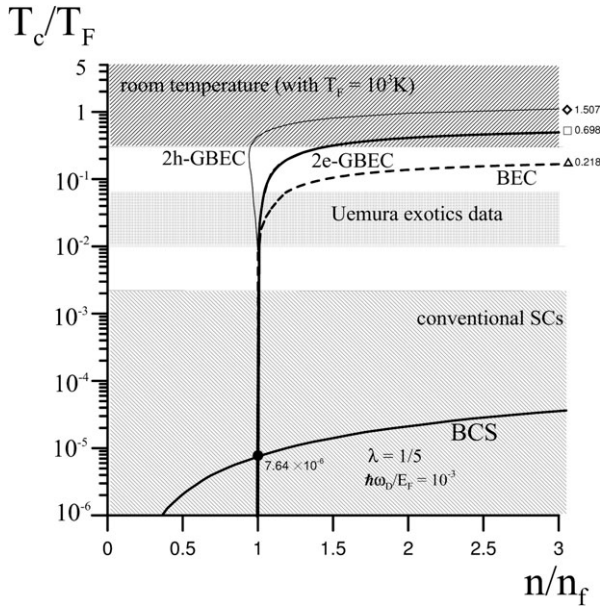

Figure 2. Phase boundaries of pure GBEC of 2h-CPs (thin curve) and of 2e-CPs (thick full curve) compared to the standard BEC curve (dashed) and the BCS, for a BCS model interaction creating the CPs, all for BCS model interaction dimensionless parameters $\lambda = 1/5$ and $\hbar\omega_D/E_F = 10^{-3}$ vs. dimensionless charge-carrier densities n/n_f with n_f as defined in text. Exotics data are from Ref. [27]. Here and in text $\hbar\omega_D$ is the Debye energy associated with the ionic lattice while E_F is the Fermi energy of the electron gas. Values indicated by the diamond, square and triangle, correspond to the limit values of T_c obtained for $n/n_f \to \infty$.

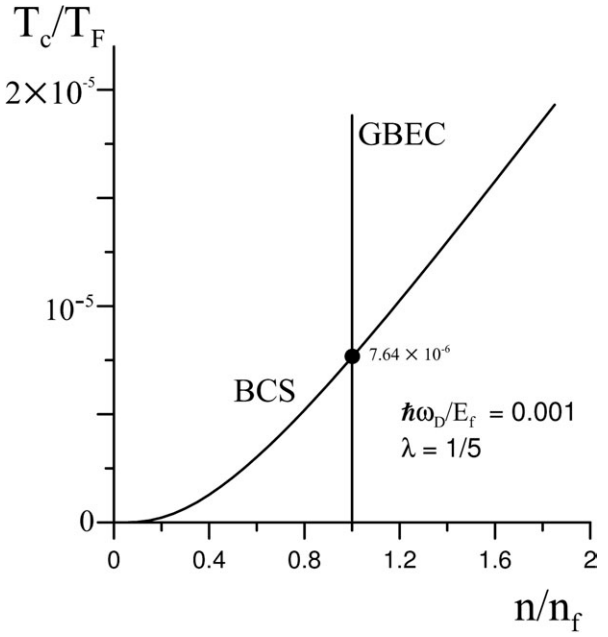

Figure 3. Phase boundaries of GBEC where it shows the sharp linear rise in n/n_f of T_c predicted by the GBEC formalism, in contrast with the exponential rise predicted by BCS theory.

at lower temperatures three condensed phases appear: two pure phases of 2e-CP- and 2h-CP-BE-condensed states and one mixed phase with arbitrary proportions of both kinds of BE-condensed CPs. Figure 2 shows the phase boundaries for the specific set of BCS interaction parameters $\lambda = 1/2$ and $\hbar\omega_D = 10^{-3}E_F$. Figure 3 shows the sharp linear rise in n/n_f of T_c predicted by the GBEC formalism, this contrasts with the exponential rise predicted by BCS theory.

In addition, the multiple GBEC-predicted T_c values at the same n/n_f would seem to suggest a possible explanation, to be explored in the near future, for the intriguing experimental fact emphasized by Hirsch (Ref. [28] section 6) that regardless of whether charge carriers above T_c are holes or electrons, they are always electrons below T_c.

Conclusions

The GBEC formalism therefore predicts the observed[29] linear rise of T_c with charge-carrier density (e.g., doping, as in underdoped cuprates such as YBaCuO) in contrast with the exponential rise of BCS theory. The hopefully practical outcome of the BCS-BEC unification ensuing from that formalism is enhancement in T_c by up to four orders-of-magnitude in 3D. These enhancements fall within empirical ranges for 2D and 3D "exotic" SCs, whereas BCS T_c values remain much lower—being within the empirical ranges for conventional, elemental SCs using standard interaction-parameter values. Lastly, room-temperature superconductivity is possible for a material with a Fermi temperature $T_F \leq 10^3$K, with the same electron-phonon[30] interaction parameters used in BCS theory for conventional SCs.

Keywords: Cooper pairs · Base-Einstein condensation · superconductors · superfluids

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[1] R. Micnas, S. Robaszkiewicz, and A. Bussmann-Holder, *Struct. Bond* **2005**, *114,* 13.
[2] R. Friedberg, T. D. Lee, H.-C. Ren, *Phys. Rev. B* **1992**, *45,* 10732.
[3] M. de Llano, V. V. Tolmachev, *Ukrainian J. Phys.* **2010**, *55,* 79.
[4] J. Bardeen, L. N. Cooper, J. R Schrieffer, *Phys. Rev.* **1957**, *108,* 1175.
[5] L. N. Cooper, *Phys. Rev.* **1956**, *104,* 1189.
[6] M. Fortes, M. A. Solís, M. de Llano, V. V. Tolmachev, *Physica C* **2001**, *364,* 95.
[7] M. de Llano, F. J. Sevilla, S. Tapia, *Int. J. Mod. Phys. B* **2006**, *20,* 2931.
[8] J. R. Schrieffer, Theory of Superconductivity; Benjamin: New York, **1964**; p.38.
[9] V. V. Tolmachev, *Phys. Lett. A* **2000**, *266,* 400.
[10] M. de Llano, V. V. Tolmachev, *Phys. A* **2003**, *317,* 546.
[11] B. S. Deaver, Jr., W. M. Fairbank, *Phys. Rev. Lett.* **1961**, *7,* 43.
[12] R. Doll, M. Näbauer, *Phys. Rev. Lett.* **1961**, *7,* 51.
[13] C. E. Gough, M. S Colclough, E. M. Forgan, R. G. Jordan, M. Keene, C. M. Muirhead, I. M. Rae, N. Thomas, J. S. Abell, S. Sutton, *Nature* **1987**, *326,* 855.
[14] S. Fujita, D. L. Morabito, *Mod. Phys. Lett. B* **1998**, *12,* 753.
[15] S. Fujita, S. Godoy, Theory of High Temperature Superconductivity; Kluwer: New York, **2001**; pp.97–98.
[16] A. J. Leggett, *Nat. Phys.* **2006**, *2,* 134.
[17] P. Ehrenfest, J. R. Oppenheimer, *Phys. Rev.* **1931**, *37,* 333.
[18] T. Matsubara, J. M. Blatt, *Prog. Theor. Phys.* **1960**, *23,* 451.

[19] R. Friedberg, T. D. Lee, *Phys. Rev. B* **1989**, *40,* 6745.
[20] R. Friedberg, T. D. Lee, H.-C. Ren, *Phys. Lett. A* **1991**, *152,417,* 423.
[21] P. Nozières, S. Schmitt-Rink, *J. Low. Temp. Phys.* **1985**, *59,* 195.
[22] H. Fröhlich, *Proc. R. Soc. (London),* **1952**, *215,* 291.
[23] A. L. Fetter, J. D. Walecka, Quantum Theory of Many-Particle Systems; McGraw-Hill: New York, **1971**.
[24] N. N. Bogoliubov, *J. Phys. (USSR),* **1947**, *11,* 23.
[25] J. Ranninger, R. Micnas, S. Robaszkiewicz, *Ann. Phys. Fr.* **1988**, *13,* 455.
[26] J. F. Annett, Superconductivity, Superfluids and Condensates, Oxford University Press: UK, **2004**; pp.70.
[27] (a) Y. J. Uemura, *J. Phys.: Condens. Matter* **2004**, *16,* S4515; (b) Y. J. Uemura, *Phys. B* **2006**, *374,* 1.
[28] J. Hirsch, *Int. J. Mod. Phys. B* **2009**, *23,* 3035.
[29] D. M. Broun et al., *Phys. Rev. Lett.* **2007**, *99,* 237003.
[30] V. Z. Kresin, S. A. Wolf, *Rev. Mod. Phys.* **2009**, *81,* 481.

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