Pre-formed Cooper pairs and Bose-Einstein condensation in cuprate superconductors

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Abstract

A two-dimensional (2D) assembly of noninteracting, temperature-dependent, pre-formed Cooper pairs in chemical/thermal equilibrium with unpaired fermions is examined in a binary boson-fermion statistical model as the Bose-Einstein condensation (BEC) singularity temperature \( T_c \) is approached from above. Compared with BCS theory (which is not a BEC theory) substantially higher \( T_c \)'s are obtained without any adjustable parameters, that fall roughly within the range of empirical \( T_c \)'s for quasi-2D cuprate superconductors.

A possible interpretation of the “pseudo-gap” observed in some superconductors above \( T_c \) is that it arises simultaneously with the formation of “pre-formed” Cooper pairs (CPs). We propose here that such objects emerge naturally as the nonzero-total (or, -center-of-mass) momentum (CMM) CPs that are entirely neglected in ordinary BCS theory.

Consider a 2D system of \( N \) fermions of mass \( m \) confined in a square of area \( L^2 \) and interacting pairwise via the BCS model interaction \( V_{\mathbf{k},\mathbf{k}'} = -V \) when \( \mu(T) - \hbar \omega_D < \epsilon_{k_1} (= \hbar^2 k_1^2/2m) \) and \( \epsilon_{k_2} < \mu(T) + \hbar \omega_D \), and zero otherwise, where \( \mathbf{k} \equiv \frac{1}{2}(\mathbf{k}_1 - \mathbf{k}_2) \) is the relative wavevector of the two particles; \( V_{\mathbf{k},\mathbf{k}'} \) the 2D double Fourier integral of the underlying non-local interaction \( V(\mathbf{r},\mathbf{r}') \) in the relative coordinate \( \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \); \( \mu(T) \) the ideal Fermi gas (IFG) chemical potential which at \( T = 0 \) becomes the Fermi energy \( E_F \equiv \hbar^2 k_F^2/2m \) with \( k_F \) the Fermi wavenumber; \( 2\hbar \omega_D \equiv \hbar^2 k_D^2/m \) the energy width of the annulus centered around the Fermi circle and where the interaction is nonzero, with \( \omega_D \) the Debye frequency. For \( V > 0 \) this model interaction mimics the net effect of an attractive electron-phonon interaction overwhelming the interfermion Coulomb repulsions.

If \( \hbar \mathbf{K} = \hbar(\mathbf{k}_1 + \mathbf{k}_2) \) is the CMM of a CP, let \( E_K \) be its total energy (besides the CP rest-mass energy). The original eigenvalue CP \([\text{II}]\) equation for a pair of fermions at \( T = 0 \) immersed in a background of \( N - 2 \) inert, spectator fermions lying within a (sharp) Fermi circular perimeter of radius \( k_F \), is then

\begin{equation}
1 = V \sum_{\mathbf{k}} \frac{\theta(k_1 - k_F) \theta(k_2 - k_F)}{2\epsilon_{\mathbf{k}} + \hbar^2 K^2 / 4m - E_K}, \tag{1}
\end{equation}

where \( \theta(x) \) is the Heaviside unit step function, and the prime on the summation sign denotes the conditions \( k_{1,2} \equiv |\frac{1}{2}\mathbf{K} \pm \mathbf{k}| < (k_F^2 + k_D^2)^{1/2} \) ensuring that our pair of fermions above the Fermi “surface” cease interacting beyond the annulus of energy width \( 2\hbar \omega_D \), thereby restricting the summation over \( \mathbf{k} \) for a given fixed \( \mathbf{K} \). Without these restrictions \([\text{II}]\) would just be the Schrödinger equation in momentum space for the pair. Setting \( E_K = 2E_F - \Delta_K \), the pair is bound if \( \Delta_K > 0 \), and \([\text{II}]\) becomes an eigenvalue equation for the (positive) pair binding energy \( \Delta_K \). Our \( \Delta_K \) and \( \Delta_0 \) should not be confused with the BCS energy gap \( \Delta(T) \) at
$$T = 0. \text{ Let } \lambda \equiv g(E_F)V \geq 0 \text{ be the usual BCS dimensionless coupling constant. Here } g(E_F) \text{ is the electronic density-of-states (for each spin) at the Fermi surface in the normal (i.e., interactionless) state, which in 2D is } g(\epsilon) = L^2m/2\pi \hbar^2 \equiv g, \text{ a constant. The Cooper equation (1) for the unknown quantity } \Delta_K \text{ was analyzed in Ref. [2]. For zero CMM, } K = 0, \text{ it becomes a single elementary integral, with the familiar solution } \Delta_0 = 2\hbar \omega_D/(e^{2/\lambda} - 1) \text{ valid for all coupling } \lambda. \text{ For small } K \text{ one determines [3] for weak coupling, } \lambda \to 0, \text{ that}

$$

$$\Delta_K \rightarrow \Delta_0 - \frac{2}{\pi} \hbar v_F K + O(K^2) \quad (2)$$

$$where \ h v_F \equiv \sqrt{2E_F/m} \text{ is the Fermi velocity. This linear dispersion relation is the 2D analog of the 3D result discussed as far back as 1964 in Ref. [3], p. 33 (see also, Ref. [4], p. 336, and [5]) but with the 2D coefficient } 2/\pi \text{ in [3] replaced by 1/2. Though commonly confused with the Anderson-Bogoliubov-Higgs (ordinary) sound mode, the linear-dispersion result (2) corresponds to real, moving (preformed) CPs and is distinct from the zero-coupling ABH (indeed, IFG) phonons described by } \hbar v_F K/\sqrt{3}. \text{ A general many-body formalism unambiguously exhibiting [6] this distinction involves solving the Bethe-Salpeter equation for Cooper pairing based not on the IFG, as above, but on the BCS ground-state in a Green's functions scheme allowing holes on a par with particles.}

For } N_B \text{ ordinary bosons of mass } m_B \text{ and energy } \epsilon_K = C_s K^s \text{ with } s > 0 \text{ and } C_s \text{ a constant, a temperature singularity appears at } T_c \neq 0 \text{ for any } d \text{ dimension } d > s \text{ in the number equation } N_B = \sum_K \rho_K B(e^\epsilon_K - B^s + 1)^{-1} \text{ at vanishing bosonic chemical potential } \mu_B \leq 0 \text{ when the number of } K = 0 \text{ bosons just ceases to be negligible upon cooling. It is given [7] by}

$$T_c = \frac{C_s}{k_B} \left[ \frac{s \frac{\Gamma(d/2)(2\pi)^d n_B}{2\pi^{d/2} \Gamma(d/s) g_{d/s}(1)}}{s/d} \right]^{-1} \quad (3)$$

$$with \ n_B \equiv N_B/L^d \text{ the boson particle density, and } g_{d/s}(z) \text{ the usual Bose integrals expressible as the series}

$$g_{\sigma}(z) = \sum_{l=1}^\infty \frac{z^l}{l!} \rightarrow \zeta(\sigma), \quad (4)$$

$$where \ \zeta(\sigma) \text{ the Riemann zeta function of order } \sigma. \text{ The last identification in [4] holds when } \sigma > 1 \text{ for which } \zeta(\sigma) < \infty, \text{ while the series } g_{\sigma}(1) \text{ diverges for } \sigma \leq 1, \text{ thus giving } T_c = 0 \text{ for } d \leq 2. \text{ For } s = 2 \text{ and } d = 3 \text{ one has } \zeta(3/2) \simeq 2.612, \text{ and since } C_2 \equiv \hbar^2/2m_B \text{ (3) then reduces to the familiar formula } T_c \simeq 3.31 \hbar^2 n_B^{2/3}/m_B k_B \text{ of "ordinary" Bose-Einstein condensation (BEC). On the other hand, for either particle or hole bosons with (positive) excitation energy } \epsilon_K \equiv \Delta_0 - \Delta_K \text{ given asymptotically by the linear term in (2) for all } K, \text{ we have } C_1 \equiv a(d) \hbar v_F \text{ where [1] } a(d) = 1, 2/\pi \text{ and } 1/2 \text{ for } d = 1, 2 \text{ and } 3, \text{ respectively. Now } T_c \text{ is nonzero for all } d > 1- \text{which is precisely the dimensionality range of all known superconductors including the quasi-1D organo-metallic (Bechgaard) salts [11].}$$

The number of bosons in the boson-fermion mixture in chemical/thermal equilibrium turn out [11] to be temperature-dependent, and it is in conserving the fermion number that the singularity arises. As in the case of the pure boson gas (3), a linear rather than a quadratic dispersion relation is needed to obtain BEC in exactly 2D. All this emerges in a statistical model for the ideal binary gas mixture of bosons (the CPs) and unpaired (both pairable and unpairable) fermions in chemical equilibrium [12]. Thermal pair-breaking of the bosons into unpaired pairable fermions is explicitly allowed. At any } T \text{ the total number of fermions in 2D is } N = L^2k_F^2/2\pi = N_1 + N_2, \text{ and is just the number of non-interacting (i.e., unpairable) fermions } N_1 \text{ plus the number of pairable ones } N_2. \text{ The unpairable fermions obey the usual Fermi-Dirac (FD) distribution with the IFG chemical potential } \mu. \text{ On the other hand, the } N_2 \text{ pairable fermions are simply those in the interaction shell of energy width } 2\hbar \omega_D \text{ so that}

$$N_2 = 2 \int_{\mu - \hbar \omega_D}^{\mu + \hbar \omega_D} dx \frac{g(\epsilon)}{e^{\beta(\epsilon - \mu)} + 1} = 2g(\epsilon) \hbar \omega_D, \quad (5)$$

$$where \ \beta \equiv (k_B T)^{-1}, \text{ since a constant } g(\epsilon) \text{ renders the remaining integral exact. At any inter-fermionic coupling and temperature these fermions form an ideal mixture of pairable but unpaired fermions plus CPs that are created near the single-fermion energy } \mu(T), \text{ with binding energy } \Delta_K(T) \geq 0 \text{ and total energy}

$$E_K(T) = 2\mu(T) - \Delta_K(T). \quad (6)$$

This generalizes the } T = 0 \text{ definition } E_K \equiv 2E_F - \Delta_K \text{ given below (1).}

The Helmholtz free energy } F \equiv E - TS, \text{ where } E \text{ is the internal energy and } S
the entropy, for this binary gas “composite boson/pairable-but-unpaired-fermion system” at $T \leq T_c$ is then readily constructed in terms of: a) $n_2(e)$, the average number of unpaired but pairable fermions with energy $e$; b) $N_{B,0}(T)$, the number of (bosonic) CPs with zero CMM at temperature $T$; and c) $N_{B,K}(T)$, that number of excited pre-formed CPs (i.e., with arbitrary nonzero CMM $K$) and a cutoff $K_0$ physically defined by $\Delta_{K_0} \equiv 0$ denoting the value of $K$ beyond which a CP breaks up. The free energy $F_{2}$ of the pairable fermions is to be minimized subject to the constraint that $N_2$ is conserved. If $N_{20}(T)$ is the number of pairable but unpaired fermions, the relevant number equation for the pairable (i.e., active) fermions is then

$$N_2 = N_{20}(T) + 2[N_{B,0}(T) + N_{B,0 < K < K_0}(T)] = N_{20}(T) + 2N_B(T),$$  \hspace{1cm} (7)$$

where $N_{B,0 < K < K_0}(T)$ denotes the total number of “excited” bosonic pairs (namely with CMM such that $0 < K < K_0$), i.e., $N_{B,0 < K < K_0}(T) = \sum_{0 < K < K_0} N_{B,K}(T)$. At $T = 0$ two distinct coupling regimes emerge: a) for $\Delta_0 < 2h\omega_D$ or for $\lambda \leq 2\ln 2 \simeq 2.89$, we have that $N_{20}(T) = 0$; g$(2h\omega_D - \Delta_0)$; while b) for $\Delta_0 > 2h\omega_D$ (or $\lambda \simeq 2.89$), $N_{20}(0)$ is identically zero. Hence, the number of bosons $N_B(0)$ at $T = 0$ from (7) is just $N_B(0) = \frac{1}{2}[N_2 - N_{20}(0)]$. Using F for the fractional number of pairable fermions that are actually paired at $T = 0$, namely $2N_B(0)/N_2 = 1 - N_{20}(0)/N_2$, becomes simply $\Delta_0/2h\omega_D = (e^{2/\lambda} - 1)^{-1} \rightarrow e^{-2/\lambda} as \lambda \rightarrow 0$, for $\lambda \leq 2/\ln 2 \simeq 2.89$, and unity for $\lambda \geq 2/\ln 2$. As $N_B(0) = \frac{1}{2}g\Delta_0$ for $\lambda \leq 2.89$, only those fermions in an energy shell of width $0.5\Delta_0$ around the Fermi surface actually pair at $T = 0$, for $\lambda \geq 2.89$ all pairable fermions pair up since then $N_B(0) = g\hbar\omega_D \equiv \frac{1}{2}N_2$. For $T > 0$, $2N_B(T)/N_2 = 1 - N_{20}(T)/N_2$ decreases with $T$, provided one knows $\Delta_0(T)$ for any $T > 0$ and ascertains that it decreases. For $T > 0$, the $\theta(k_1 - k_F) \equiv \theta(\xi_k - E_F)$ in $f$ becomes $1 - n(\xi_k)$, where $n(\xi_k) \equiv (e^{\beta\xi_k} - 1)^{-1}$ is the FD distribution with $\xi_k \equiv \xi_1 - \mu(T)$, with the IFG chemical potential $\mu(T)$ in 2D given exactly by $\mu(T) = \beta^{-1}\ln(e^{\beta E_F} - 1) \rightarrow E_F$ as $T \rightarrow 0$. Similarly for $\theta(k_2 - k_F)$. Since $k_1 = k_2$ implies that $\xi_{k_1} = \xi_{k_2}$, $f$ then leads to a simple generalization to nonzero $T$ of the $K = 0$ CP equation,

$$1 = \lambda \int_{0}^{h\omega_D} d\xi (e^{-\beta\xi} + 1)^{-2} [2\xi + \Delta_0(T)]^{-1}. \hspace{1cm} (8)$$

Numerical solution shows $\Delta_0(T)$ to indeed be monotonic-decreasing in $T$ for any fixed $\lambda$ and $h\omega_D$. Further, the solution of $\Delta_0(T^*) = 0$ is, by inspection, $T^* = \infty$; this infinite “de-pairing” temperature is unrealistic and undoubtedly an artifact of the simplest version (1) of Cooper pairing used here as a starting point; see, however, Ref. $i$.

Modeling our system as a pure boson gas of CPs (i.e., neglecting the background unpaired fermions) but with a temperature-dependent number density $n_B(T)$ converts the explicit $T_c$-formula (3) into an implicit one. For $s = 1$ and $d = 2$ it becomes, since $g_2(1) \equiv \zeta(2) = \pi^2/6$,

$$T_c = \frac{4\sqrt{3} \hbar v_F}{\pi^{3/2} k_B} \frac{n_B(T_c)}{20}. \hspace{1cm} (9)$$

This requires $n_B(T) = N_B(T)/L^2$ which in turn requires $\Delta_0(T)$ as determined from $(5)$, and follows from the expression $2N_B(T)/N_2 = 1 - N_{20}(T)/N_2$. Solving this self-consistently with (7) for $\lambda = 1/2$ gives the remarkably constant value $T_c/T_F \simeq 0.004$, where $T_F \equiv E_F/k_B$, over the entire range of $\nu \equiv h\omega_D/E_F$ values 0.03 – 0.07 typical of cuprate superconductors. On the other hand, the BCS formula $T_{BCS} = 1.13\Theta_D e^{-1/\lambda}$ with $\lambda = 1/2$ gives $T_c/T_F = 0.005$ to 0.011 over the same range of $\nu$ values. Obviously, both sets of predictions are too small compared with the empirical cuprate range $T_c/T_F \simeq 0.03 – 0.09$ $[13]$. The exact $T_c$ without neglecting the background unpaired fermions requires the exact CP excitation energy dispersion relation $\varepsilon_k(T) \equiv \Delta_0(T) - \Delta_K(T)$ which is neither precisely linear in $K$ nor independent of $T$. To determine $\Delta_K(T)$ $e$ we need a working equation that generalizes Ref. $[2]$ for $T > 0$ via the new CP eigenvalue equation $(8)$. At $T = T_c$ both $N_{B,0}(T_c) \simeq 0$ and $\mu(T_c) \simeq 0$ so that one gets $f$ the implicit $T_c$-equation for the binary gas mixture

$$1 = \frac{\bar{T}_e}{\nu} \ln \left[ \frac{1 + e^{-(\Delta_0(T_c)/2-\nu)/\bar{T}_e}}{1 + e^{-(\Delta_0(T_c)/2+\nu)/\bar{T}_e}} \right] + 8(1 + \nu) \frac{\kappa}{\nu} \times \int_{0}^{\kappa}(\bar{T}_e) \frac{d\kappa}{e^{\Delta_0(T_c)-\Delta_K(T_c)}}/\bar{T}_e - 1, \hspace{1cm} (10)$$

where quantities with tildes are in units of $E_F$ or $T_F$; $\kappa \equiv K/(k_F^2 + k_D^2)^{1/2}$ with $k_D$ defined through $h\omega_D \equiv k_F^2/2m$ and $\nu \equiv \Theta_D/T_F$. To obtain $T_c$ from the finite-$T$ dispersion relation one must numerically solve four equations self-consistently for each $\lambda$ and $\nu$, namely $(10)$ in
conjunction with (8) for $\Delta_0(T)$, and Eq. (35) of Ref. [2] for both $\Delta_r(T)$ and the breakup value $\kappa_0(T_c)$. For $\lambda = 1/2$ and the range of $\nu$ values $0.03 - 0.07$ typical of cuprates, the resulting $T_c/T_F$ falls within the aforementioned empirical range $0.03 - 0.09$ [3]. For cuprates $d \approx 2.03$ has been suggested [4] as more realistic since it reflects inter-CuO-layer couplings, but our results in that case would be very close to those for $d = 2$ since, e.g., from (3) $T_c$ for $s = 1$ (but not for 2) varies little with $d$ around $d = 2$. In fact, if $m_{B\perp}$ and $m_B$ are the boson masses perpendicular and parallel, respectively, to the cuprate planes, an “anisotropy ratio” $m_B/m_{B\perp}$ varied from 0 to 1 allows “tuning” $d$ continuously from 2 to 3.

Other boson-fermion models [5-19] have been introduced, some even addressing d-wave interaction effects as opposed to the pure s-wave considered here, and some also focus on the pseudogap. But calculating cuprate $T_c$ values in quasi-2D without adjustable parameters has not been attempted, and indeed $T_c \equiv 0$ is predicted in exactly 2D.

In summary, a simple statistical model treating pre-formed CPs with both zero and nonzero CMM as non-interacting bosons in chemical/thermal equilibrium with unpaired fermions is proposed that gives rise to a boson number that is strongly coupling- and temperature-dependent. Since the CP dispersion relation is approximately linear for nonzero CMM, it exhibits a BEC of zero-CMM pairs at precisely 2D. In contrast to both BCS theory—which is not a BEC theory—and simpler BE models excluding either the breakable character of the pre-formed CPs or the presence of unpaired fermions, exact $T_c$’s for the boson-fermion binary mixture based upon the exact CP dispersion relation are found in rough agreement with empirical cuprate values with no adjustable parameters.

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