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Towards room-temperature superconductivity

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By taking advantage of a stability criterion established recently, the critical temperature T_c is reckoned with help of the microscopic parameters, characterising the normal and superconducting electrons, namely the independent-electron band structure and a *repulsive* two-electron force. The emphasis is laid on the sharp T_c dependence upon electron concentration and inter-electron coupling, which might offer a practical route toward higher T_c values and help to understand why high-T_c compounds exhibit such remarkable properties.

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The BCS theory[1], despite its impressive success, does not enable one to predict[2] superconductivity occurring in any metallic compound. Such a drawback ensues from an *attractive* interaction, assumed to couple electrons together, which is not only at loggerheads with the sign of the Coulomb repulsion but in addition leads to questionable conclusions to be discussed below. Therefore this work is intended at investigating the T_c dependence upon the parameters, characterising the motion of electrons correlated together through a *repulsive* force, within the framework of a two-fluid picture[3] to be recalled below.

The conduction electrons comprise bound and independent electrons, in respective temperature dependent concentration $c_s(T), c_n(T)$, such that $c_0 = c_s(T) + c_n(T)$ with c_0 being the total concentration of conduction electrons. They are organized, respectively, as a many bound electron[4] (MBE) state, characterised by its chemical potential $\mu(c_s)$, and a Fermi gas[5] of Fermi energy $E_F(T, c_n)$. The Helmholz free energy of independent electrons per unit volume F_n and E_F on the one hand, and the eigenenergy per unit volume $\mathcal{E}_s(c_s)$ of bound electrons and μ on the other hand, are related[5, 6], respectively, by $E_F = \frac{\partial F_n}{\partial c_n}$ and $\mu = \frac{\partial \mathcal{E}_s}{\partial c_s}$. Then a stable equilibrium is conditioned[7] by Gibbs and Duhem's law

$$E_F(T, c_n(T)) = \mu(c_s(T)) \quad , \tag{1}$$

which expresses[6] that the total free energy $F_n + \mathcal{E}_s$ is minimum provided $\frac{\partial E_F}{\partial c_n} + \frac{\partial \mu}{\partial c_s} > 0$. Noteworthy is that $\frac{\partial \mu}{\partial c_s} < 0$ has been shown to be a prerequisite for persistent currents[7], thermal equilibrium[4], the Josephson effect[8] and a stable[3] superconducting phase. Likewise, Eq.(1) reads[4, 7] for $T = T_c$

$$E_F(T_c, c_0) = \mu(c_s = 0) = \varepsilon_b/2 \quad , \tag{2}$$

with ε_b being the energy of a *bound* electron pair[4]. Note that Eqs.(1,2) are consistent with the superconducting transition being of second order[6], whereas it has been shown[4] to be of first order at $T < T_c$ ($\Rightarrow E_F(T, c_0 - c_s) \neq \mu(c_s)$), if the sample is flown through by a finite current.

The binding energy[4] of the superconducting state $E_b(T < T_c)$ has been worked out as

$$E_b(T) = \int_T^{T_c} \left(C_s(u) - C_n(u)\right) du \quad ,$$

with $C_s(T), C_n(T)$ being the electronic specific heat of a superconductor, flown through by a vanishing current[4] and that of a degenerate Fermi gas[5]. A stable phase ($\Rightarrow E_b > 0$) requires $C_s(T_c) > C_n(T_c)$, which can be secured[3] *only* by fulfilling the following condition

$$\frac{\partial E_F}{\partial c_n}(T_c, c_0) = -\frac{\partial \mu}{\partial c_s}(0), \quad \rho'(E_F(T_c, c_0)) > 0 \quad , \tag{3}$$

with $\rho(\epsilon), \epsilon$ being the independent electron density of states and one-electron energy, respectively, and $\rho' = \frac{d\rho}{d\epsilon}$.

Since the remaining analysis relies heavily on Eqs.(2,3), explicit expressions are needed for $E_F(T_c, c_0)$, $\frac{\partial E_F}{\partial c_n}(T_c, c_0)$, ε_b, $\frac{\partial \mu}{\partial c_s}(0)$. Because the independent electrons make up a degenerate Fermi gas ($\Rightarrow T << E_F/k_B$ with k_B being Boltzmann's constant), applying the Sommerfeld expansion[5] up to T^2 yields

$$\begin{aligned} E_F(T_c, c_0) &= E_F(0, c_0) - \frac{\rho'}{\rho}\frac{(\pi k_B T_c)^2}{6} \\ \frac{\partial E_F}{\partial c_n}(T_c, c_0) &= \left(\rho + \rho''\frac{(\pi k_B T_c)^2}{6}\right)^{-1} \end{aligned} \quad , \tag{4}$$

with $\rho = \rho(E_F(0, c_0)), \rho' = \frac{d\rho}{dE_F}(E_F(0, c_0)), \rho'' = \frac{d^2\rho}{dE_F^2}(E_F(0, c_0))$. As for ε_b, $\frac{\partial \mu}{\partial c_s}(0)$, a truncated Hubbard Hamiltonian H_K, introduced previously[9–11], will be used. The main features of the calculation[4] are summarised below for self-containedness.

The independent electron motion is described by the Hamiltonian H_d

$$H_d = \sum_{k,\sigma} \epsilon(k) c^+_{k,\sigma} c_{k,\sigma} \quad .$$

$\epsilon(k), k$ are the one-electron energy ($\epsilon(k) = \epsilon(-k)$) and a vector of the Brillouin zone, respectively, $\sigma = \pm$ is the electron spin and the sum over k is to be carried out over the whole Brillouin zone. Then $c^+_{k,\sigma}, c_{k,\sigma}$ are creation and annihilation operators on the Bloch state $|k,\sigma\rangle$

$$|k,\sigma\rangle = c^+_{k,\sigma}|0\rangle \quad , \quad |0\rangle = c_{k,\sigma}|k,\sigma\rangle \quad ,$$

with $|0\rangle$ being the no electron state. The Hamiltonian H_K reads then

$$H_K = H_d + \frac{U}{N}\sum_{k,k'} c^+_{k,+}c^+_{K-k,-}c_{K-k',-}c_{k',+} \quad ,$$

with $N >> 1, U > 0$ being the number of atomic sites, making up the three-dimensional crystal, and the Hubbard constant, respectively. Note that the Hamiltonian used by Cooper[12] is identical to $H_{K=0}$, but with $U < 0$.

H_K sustains[4] a single *bound* pair eigenstate, the energy $\varepsilon_b(K)$ of which is obtained by solving

$$\frac{1}{U} = \frac{1}{N}\sum_k \frac{1}{\varepsilon_b(K) - \varepsilon(K,k)} = \int_{-t_K}^{t_K} \frac{\rho_K(\varepsilon)}{\varepsilon_b(K) - \varepsilon} d\varepsilon. \quad (5)$$

$\pm t_K$ are the upper and lower bounds of the two-electron band, i.e. the maximum and minimum of $\varepsilon(K,k) = \epsilon(k) + \epsilon(K-k)$ over k, whereas $\rho_K(\varepsilon)$ is the corresponding two-electron density of states, taken equal to

$$\rho_K(\varepsilon) = \frac{2}{\pi t_K}\sqrt{1 - \left(\frac{\varepsilon}{t_K}\right)^2} \quad .$$

The dispersion curves $\varepsilon_b(K)$ are plotted in Fig.1. Though Eq.(5) is identical to the equation yielding the Cooper pair energy[12], their respective properties are quite different :

- the data in Fig.1 have been calculated with $U > 0$, rather than $U < 0$ favoured by Cooper[12] and BCS[1], because, due to the inequality[4] $U\frac{\partial \mu}{\partial c_s} < 0$, choosing $U < 0$ entails $\frac{\partial \mu}{\partial c_s} > 0$, which has been shown *not* to be consistent with persistent currents[7], thermal equilibrium[4], the Josephson effect[8] and occurence[3] of superconductivity. As a further consequence of $U > 0$, $\varepsilon_b(K)$ shows up in the upper gap of the two-electron band structure ($\Rightarrow \varepsilon_b(K) > t_K$) rather than in the lower gap ($\Rightarrow \varepsilon_b(K=0) < -t_K$) in case of the Cooper pair[12]. Nevertheless the bound pair is thermodynamically stable, because every one-electron state of energy $< E_F(T_c, c_0)$, is actually occupied, so that, due to Pauli's principle, a bound electron pair of energy $\varepsilon_b(K) = 2E_F(T_c, c_0)$, according to Eq.(2), cannot decay into two one-electron states $\epsilon(k) < E_F, \epsilon(K-k) < E_F$;
- a remarkable feature in Fig.1 is that $\varepsilon_b(K) \to t_K$ for $U \to t_K/2$, so that there is *no* bound pair for $U < t_K/2$ (accordingly, the dashed curve is no longer defined in Fig.1 for $\frac{Ka}{\pi} < .13$), in marked contrast with the opposite conclusion drawn by Cooper[12], that there is a Cooper pair, even for $U \to 0$. This discrepancy results from the three-dimensional Van Hove singularities, showing up at both two-electron band edges $\rho_K(\varepsilon \to \pm t_K) \propto \sqrt{t_K - |\varepsilon|}$, unlike the two-electron density of states, used by Cooper[12] which is constant and thence displays no such singularity. Likewise the width of Cooper's two-electron band is equal to a Debye phonon energy $2t_{K=0} = \omega_D \approx 30meV << E_F \approx 3eV$. Hence the resulting small concentration of superconducting electrons, $\frac{c_s(T=0)}{c_0} \approx \frac{\omega_D}{E_F} \approx .01$, entails that London's length should be at least 10 times larger than observed values[13–16];
- at last Cooper's assumption $U < 0$ implies $\varepsilon_b/2 \neq E_F(T_c)$, which is typical of a first order transition but runs afoul at all measurements, proving conversely the superconducting transition to be of second order ($\Rightarrow \varepsilon_b/2 = E_F(T_c)$ in accordance with Eq.(2)).

The bound pair of energy $\varepsilon_b(K)$ turns, at finite concentration c_s, into a MBE state, characterised by $\mu(c_s)$. Its properties have been calculated thanks to a variational procedure[4], displaying several merits with respect to that used by BCS[1] :

- it shows that $\mu(0) = \varepsilon_b/2$;
- the energy of the MBE state has been shown to be exact for $|U| \to \infty$;
- an analytical expression has been worked out for $\frac{\partial \mu}{\partial c_s}(K, c_s = 0)$ as :

$$\frac{\partial \mu}{\partial c_s}(K, c_s = 0) = -\frac{\int_{-t_K}^{t_K} \frac{\rho_K(\varepsilon)}{(\varepsilon_b(K)-\varepsilon)^3} d\varepsilon}{2\left(\int_{-t_K}^{t_K} \frac{\rho_K(\varepsilon)}{(\varepsilon_b(K)-\varepsilon)^2} d\varepsilon\right)^2} \quad . \quad (6)$$

The T_c dependence on c_0 will be discussed by assigning to $\rho(\epsilon)$ the expression, valid for free electrons

$$\rho(\epsilon) = \eta\sqrt{\epsilon - \epsilon_b} \Rightarrow c_0 = \frac{2}{3}\eta\left(E_F(0, c_0) - \epsilon_b\right)^{\frac{3}{2}} \quad , \quad (7)$$

with $\eta = \frac{\sqrt{2}m^{\frac{3}{2}}V}{\pi^2\hbar^3}$, whereas $\epsilon_b, m, V = 17Å^3$ stand for the bottom of the conduction band, electron mass and volume of the unit-cell, respectively.

With help of Eq.(4), Eqs.(2,3) can be recast into a system of two equations

$$\begin{array}{l} E_F(0, c_0) - \frac{\rho'}{\rho}\frac{(\pi k_B T_c)^2}{6} - \frac{\varepsilon_b(K)}{2} = 0 \\ \left(\rho + \rho''\frac{(\pi k_B T_c)^2}{6}\right)^{-1} + \frac{\partial \mu}{\partial c_s}(K, c_s = 0) = 0 \end{array} \quad , \quad (8)$$

to be solved for the two unknowns $c_0(T_c), t_K(T_c)$ with T_c being dealt with as a disposable parameter.

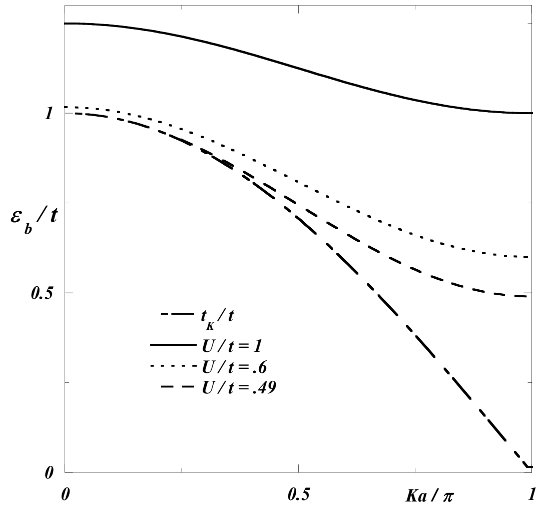

FIG. 1. Dispersion curves of t_K as a dashed-dotted line and of $\varepsilon_b(K)$ as solid, dashed and dotted lines, associated with various U values, respectively; those data have been obtained with $t_K = t\cos(Ka/2)$, where t, a are the one-electron bandwidth and the lattice parameter, respectively.

To that end, starting values are assigned to U, t_K, which gives access to $\varepsilon_b(K), \frac{\partial \mu}{\partial c_s}(K, c_s = 0))$ and thence to $E_F(0, c_0), \epsilon_b$ and finally to c_0, owing to Eqs.(2,3,7). Those values of c_0, t_K are then fed into Eqs.(8) to launch a Newton procedure, yielding the solutions $c_0(T_c), t_K(T_c)$. The results are presented in table I. Since we intend to apply this analysis to high-T_c compounds[17], we have focused upon low concentrations $c_0 < 0.2$, which entails, in view of Eqs.(4,7), that $\left|\frac{\partial \mu}{\partial c_s}\right|$ takes a high value. This requires in turn $\varepsilon_b(K) \to t_K$ (see Eq.(6)) and thence[4] $U \to \frac{t_K}{2}$, in agreement with $\frac{t_K}{U} \approx 2$ in table I.

A remarkable property of the data in table I is that c_0, t_K are barely sensitive to large variations of T_c, i.e. $|\delta c_0| < 10^{-3}, |\delta t_K| < 10^{-5}$ for $\delta T_c \approx 400K$. This can be understood as follows : taking advantage of Eqs.(2,4,7) results into

$$\frac{2E_F(0, c_0)}{\varepsilon_b(K)} - 1 = \frac{\pi^2}{12}\left(\frac{k_B T_c}{\Delta(T_c)}\right)^2 \quad ,$$

which, due to $\frac{dt_K}{dT_c} \approx 0, \Delta(T_c) \approx 1eV, T_c = 400K$, yields indeed $\delta c_0 = c_0(400K) - c_0(1K) \approx 10^{-3}$, in agreement with the data in table I. Such a result is significant in two respects, regarding high-T_c compounds, for which c_0 can be varied over a wide range :

- because of $\frac{dc_0}{dT_c} \approx 0$, the one-electron band structure can be regarded safely as c_0 independent, which enhances the usefulness of the above analysis;
- the large doping rate up to ≈ 0.2 is likely to give rise to local fluctuations of c_0, which, in view of the utmost sensitivity of T_c with respect to c_0, will result into a heterogeneous sample, consisting in domains, displaying T_c varying from 0 up to a few hundreds of K. Thus the observed T_c turns out to be the upper bound of a broad distribution of T_c values, associated with superconducting regions, the set of which makes up a percolation path throughout the sample. However, if the daunting challenge of making samples, wherein local c_0 fluctuations would be kept well below 10^{-4}, could be overcome, this might pave the way to superconductivity at *room* temperature.

TABLE I. Solutions $c_0(T_c), t_K(T_c), \Delta(T_c)$ $(\Delta(T_c) = E_F(0, c_0(T_c)) - \epsilon_b)$ of Eqs.(8); the unit for c_0 is the number of conduction electrons per atomic site.

$T_c(K)$	c_0	$t_K(eV)$	$\Delta(eV)$
1	0.10215	6	1.1976
400	0.10225	5.9999	1.1984

$U = 3.39eV$

$T_c(K)$	c_0	$t_K(eV)$	$\Delta(eV)$
1	0.14897	2	1.5402
400	0.14906	1.9999	1.5407

$U = 1.04eV$

$T_c(K)$	c_0	$t_K(eV)$	$\Delta(eV)$
1	0.19158	4	1.8214
400	0.19167	3.9999	1.8219

$U = 2.2eV$

The T_c dependence upon U will be analysed with

$$\rho(\epsilon) = \frac{4}{\pi t}\sqrt{1-\left(1-\frac{\epsilon}{t}\right)^2} \quad ,$$

where $2t$ stands for the one-electron bandwidth. Our purpose is to determine the unknowns $t_K(E_F, T_c), U(E_F, T_c)$ with $E_F = E_F(T = 0, c_0)$ and $c_0 = \int_0^{E_F} \rho(\epsilon) d\epsilon$. To that end, Eq.(3) will first be solved for t_K by replacing $\frac{\partial E_F}{\partial c_n}(T_c, c_0), \frac{\partial \mu}{\partial c_s}(0)$ by their expressions given by Eqs.(4,6), while taking advantage of Eq.(2). Then the obtained t_K value is fed into Eq.(5) to determine U. The results are presented in Fig.2.

It can be noticed that there is no solution for $c_0 > .75$, because $\frac{\partial E_F}{\partial c_n}(T_c, c_0) \approx \frac{1}{\rho}(E_F(0, c_0))$ and $\frac{\partial \mu}{\partial c_s}(0) > \frac{U}{2}$ decrease and increase, respectively, with increasing c_0, so that Eq.(3) can no longer be fulfilled eventually. But the most significant feature is that δU is almost insensitive to large T_c variation, except for $E_F \to 0$, i.e. for E_F close to the Van Hove singularity, located at the bottom of the band, which has two consequences :

- c_0 cannot be varied in most superconducting materials, apart from high-T_c compounds, so that U is unlikely to be equal to $U(c_0)$, indicated in Fig.2. Conversely, since high-T_c compounds allow for wide c_0 variation, c_0 can be tuned so that $U = U(c_0)$;

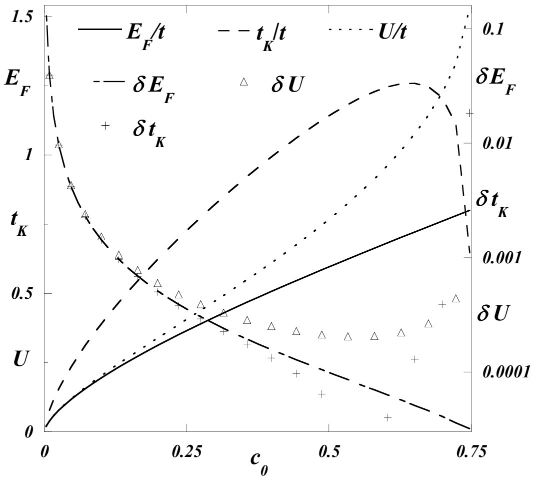

FIG. 2. Plots of $E_F(T_c, c_0), t_K(T_c, c_0), U(T_c, c_0)$ calculated for $T_c = 1K$ and $t = 3eV$; the unit for c_0 is the number of conduction electrons per atomic site; δf with $f = E_F, t_K, U$ is defined as $\delta f = \left|1 - \frac{f(300K, c_0)}{f(1K, c_0)}\right|$; the scale is linear for E_F, t_K, U but logarithmic for $\delta E_F, \delta t_K, \delta U$.

- the only possibility for a non high-T_c material to turn superconducting is then offered at the bottom of the band, because δU becomes large due to $\frac{\rho'}{\rho}(E_F \rightarrow 0) \propto \frac{1}{E_F}$ in Eq.(4). Such a conclusion, that superconductivity was likely to occur in the vicinity of a Van Hove singularity in low-T_c materials, had already been drawn[4] independently, based on magnetostriction data.

It will be shown now that $\rho(\epsilon), \rho_K(\varepsilon)$ cannot stem from the same one-electron band. The proof is by contradiction. As a matter of fact $\rho(\epsilon)$ should read in that case

$$\rho(\epsilon) = \frac{4}{\pi t}\sqrt{1 - \left(\frac{\epsilon}{t}\right)^2} \quad .$$

Hence $U > 0$ entails, in view of Fig.1 and Eq.(2), that there is $\frac{\varepsilon_b}{2} = E_F > 0$, which implies $\rho'(E_F) < 0$ in contradiction with Eq.(3). Accordingly, since the two different one-electron bands, defining respectively $\rho(\epsilon), \rho_K(\varepsilon)$, display a sizeable overlap, they should in addition belong to different symmetry classes of the crystal point group, so that superconductivity cannot be observed if there are only s-like electrons at E_F or if the point group reduces to identity. Noteworthy is that those conclusions had already been drawn empirically[2].

The critical temperature T_c has been calculated for conduction electrons, coupled via a repulsive force, within a model based on conditions, expressed in Eqs.(2,3). Superconductivity occurring in conventional materials has been shown to require $E_F(T_c)$ being located near a Van Hove singularity, whereas a practical route towards still higher T_c values has been delineated in high-T_c compounds, provided the upper bound of local c_0 fluctuations can be kept very low. The thermodynamical criterions in Eqs.(2,3) unveil the close interplay between independent and bound electrons in giving rise to superconductivity. At last, it should be noted that Eqs.(2,3) could be applied as well to any second order transition, involving only conduction electrons, such as ferromagnetism or antiferromagnetism.

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