

Strongly Correlated Superconductivity

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High-temperature superconductivity in doped Mott insulators such as the cuprates contradicts the conventional wisdom that electron repulsion is detrimental to superconductivity. Because doped fullerene conductors are also strongly correlated, the recent discovery of high-critical-temperature, presumably *s*-wave, superconductivity in C_{60} field effect devices is even more puzzling. We examine a dynamical mean-field solution of a model for electron-doped fullerenes that shows how strong correlations can indeed enhance superconductivity close to the Mott transition. We argue that the mechanism responsible for this enhancement could be common to a wider class of strongly correlated models, including those for cuprate superconductors.

In conventional superconductors, the repulsive Coulomb interaction between electrons tends to oppose phonon-mediated pairing, so that the actual critical temperature of the onset of superconductivity (T_c) decreases when electronic correlations are increased. On the contrary, in the high- T_c superconductors, strong electron-electron correlations do not suppress superconductivity but rather seem to favor it, because they are mostly poised on the brink of a repulsion-driven metal-Mott insulator transition (MIT). A recently developed approach capable of describing this transition is the so-called dynamical mean-field theory (DMFT), in which spatial fluctuations are neglected, but the time-dependent quantum fluctuations are fully described (1). As shown by DMFT, close to a Mott transition, the large Coulomb repulsion U causes the effective metallic bandwidth W to be dramatically renormalized to a quasiparticle bandwidth $W_* = ZW$, where $Z \ll 1$ is the quasiparticle residue. This small effective bandwidth corresponds to an increased quasiparticle density of states at the Fermi level $\rho = \rho_0/Z$, which could at first sight be thought to enhance the attractive coupling $\lambda = \rho V$ and thus the critical temperature (ρ_0 is the bare density of states at the Fermi energy per spin; V is the pairing attraction). However, a decreasing Z does not automatically turn into an increase of λ , because the pairing attraction V is itself renormalized down, by a factor Z^2 within Migdal-Eliashberg theory, so that the increase of U finally depresses T_c , an effect

further reinforced by a rising Coulomb pseudopotential μ_* .

An enhancement instead of a decrease of T_c with increasing Coulomb repulsion could take place if, on the contrary, the quasiparticle attraction did not get renormalized by Z and the repulsion U instead did. This is no doubt an appealing scenario, but one that is at odds with all naïve expectations based on Landau Fermi-liquid theory. In this work, we show that this scenario is actually viable. By solving a model for electron-doped C_{60} and closely examining the superconductivity arising there in the proximity of the Mott transition, we find that correlations can indeed lead to a huge enhancement of phonon-driven superconductivity with respect to the uncorrelated case. The analogy in the physics and even in the phase diagram of this fullerene model as a function of decreasing bandwidth with that of cuprates for decreasing doping draws a conceptual link between the two systems.

The Hamiltonian describing this system is

$$H = \sum_{RR'} \sum_{i,j=1}^3 \sum_{\sigma} t_{RR'}^{ij} c_{R,\sigma}^{\dagger} c_{R',j\sigma} + \frac{U}{2} \sum_R n_R n_R + H_{\text{Hund}} \quad (1)$$

where $c_{R,i\sigma}$ is the electron annihilation operator at site R in orbital i ($i = 1,2,3$) (the t_{1u} level in C_{60} is threefold degenerate) with spin σ , and $n_R = \sum_{i,\sigma} n_{R,i\sigma}$, where $n_{R,i\sigma} = c_{R,i\sigma}^{\dagger} c_{R,i\sigma}$ is the electron occupation number. We also assumed for simplicity $t_{RR'}^{ij} = \delta_{ij} t_{RR'}$. We introduce the angular momentum density operators $L_{i,R} = \sum_{j,k,\sigma} c_{R,j\sigma}^{\dagger} \hat{L}_{ijk} c_{R,k\sigma}$, with $\hat{L}_{ijk} = -i\epsilon_{ijk}$ proportional to the Levi-Civita tensor, and the spin density operators $S_{i,R} = 1/2 \sum_{\alpha,\beta} c_{R,\alpha}^{\dagger} \hat{\sigma}_{i,\alpha\beta} c_{R,\beta}$, with $\hat{\sigma}_i$ ($i = 1,2,3$) the Pauli matrices. In terms of these operators, Hund's term is $H_{\text{Hund}} = -J_H \sum_R (2\vec{S}_R \cdot \vec{S}_R + 1/2 \vec{L}_R \cdot \vec{L}_R) + 5/6 (n_R - 3)^2$.

The bare J_H is positive. However, in fullerene, the Jahn-Teller coupling of elec-

trons, and presumably also of holes (2), to the H_g molecular vibrations can reverse Hund's rules, favoring low spin and angular momentum ground states. We include this crucial electron-phonon effect by assuming $J_H < 0$, formally equivalent to treating the Jahn-Teller coupling in the antiadiabatic limit, where it can be shown to renormalize $J_H \rightarrow J_H - 3E_{JT}/4 < 0$, with E_{JT} the Jahn-Teller energy gain. The antiadiabatic approximation is justified for fullerene, where vibron frequencies are as high as 0.1 eV, to be compared with a correlation-narrowed quasiparticle bandwidth ZW , where the bare bandwidth $W \sim 0.5$ eV and a quasiparticle residue $Z \ll 1$, due to a very large U/W . In any case, the neglect of retardation disfavors superconductivity, by preventing high-energy screening of the repulsion, hence overestimating μ_* .

Following (3), we studied model 1 by DMFT (1), varying U/W , at a fixed ratio $J_H/U = -0.02$ and integer filling $\langle n \rangle = 2$ (or equivalently, $\langle n \rangle = 4$). At weak coupling, $U \ll W$, model 1 describes a metal with three 1/3-filled degenerate bands. If alone, the negative J_H would develop a superconducting *s*-wave order parameter $\Delta_R = \sum_{i=1}^3 c_{R,i\uparrow}^{\dagger} c_{R,i\downarrow}^{\dagger}$. With $J_H = 0$ and considering explicitly the electron-phonon coupling, Migdal-Eliashberg and DMFT calculations at relatively small U/W have well characterized this conventional, weakly or moderately correlated superconducting phase (3–5). However, for our present $J_H/U = -0.02$, the effective superconducting coupling $\lambda = 10\rho_0 |J_H|/3 = 0.2 \rho_0 U/3$ (ρ_0 is here the density of states per spin and band) is much smaller than the Coulomb pseudopotential $\mu_* = \rho_0 U$, and weak-coupling superconductivity is suppressed in favor of a normal metal. At strong coupling, $U \gg W$, the system is a Mott insulator. Each site is occupied by two electrons that, because $J_H < 0$, form a spin and orbital singlet, as expected in a Mott-Jahn-Teller insulator (6). This state, a kind of onsite version of the resonant valence bond (RVB) state (7), is nonmagnetic and has a gap to spin, orbital, and charge excitations. The transition between the metal and the strong-coupling Mott insulator is, however, not direct, and a superconducting phase is known to intrude in between (8). The properties of this superconducting phase are, we now find, striking.

Figure 1 shows the superconducting gap Δ , obtained as the zero-frequency anomalous self-energy, compared with the hypothetical superconducting gap calculated in standard Bardeen-Cooper-Schrieffer (BCS) theory at $U = 0$ and with the actual spin gap Δ_{spin} extracted as the edge of the main spectral peak in the dynamical spin susceptibility.

Superconductivity is seen to arise suddenly out of the normal metal upon increasing repulsion above a critical value $(U/W)_c$ (here

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0.8) and below the MIT (here at 0.9). At $(U/W)_c$ the superconducting gap initially coincides with the spin gap, as in weak-coupling BCS theory, but the two rapidly deviate. The larger spin gap merges with that of the Mott state; Δ instead reaches a peak value—a huge 1000 times the $U = 0$ BCS gap calculated for the same pairing attraction—before falling again down to zero at the MIT. The large peak value of Δ is on the order of the maximum value that could be reached at $U = 0$ if the bandwidth were comparable with $|J_H|$, which is also the condition to get the maximum T_c for a fixed unretarded attraction (9). In terms of a Landau Fermi-liquid description of the metallic phase, this suggests that the quasiparticles close to the MIT have an effective bandwidth $W_* \sim ZW \sim |J_H|$ and experience an attraction of the very same order of magnitude. If this were indeed the case, the main effect of strong correlations would be to decrease W_* and thus increase the quasiparticle mass, leaving behind only a small residual quasiparticle repulsion. If the attractive vertex remained at the same time substantially unrenormalized while $Z \rightarrow 0$, then the quasiparticle scattering amplitude would switch from repulsive at weak coupling to attractive close to the MIT. A lack of renormalization of J_H is plausible, because Hund's coupling does not compete with U but rather benefits from it. In fact, U brings the system toward the atomic limit where Hund's rules are obeyed, whereas the metallic phase is where they are violated. There is here a similarity to the $t - J$ model of cuprates, where J is also apparently unrenormalized close to the insulator, as suggested by slave boson methods (10) and by numerical calculations (11).

We found that this appealing, but thus far hypothetical, scenario is confirmed by a careful analysis of the metallic phase within Landau Fermi-liquid theory. DMFT enables a study of the normal metal even inside the superconducting region, by preventing spontaneous breaking of the gauge symmetry in the self-consistency equations and providing a full description of the quasiparticles and of their mutual interactions close to the Mott transition. The Landau functional of the model, which possesses spin SU(2) and orbital O(3) symmetry, contains here a multiplicity of Landau parameters $f^{S(A)}$, $g^{S(A)}$, and $h^{S(A)}$ (8). Defining F parameters $F^{S(A)} = 6\rho_0 f^{S(A)}/Z$, $G^{S(A)} = 12\rho_0 g^{S(A)}/Z$, and $H^{S(A)} = 4\rho_0 h^{S(A)}/Z$, dimensionless quantities that measure the strength of the interactions between quasiparticles, the susceptibilities have the standard expression $[(\chi)/(\chi^{(0)})] = [1/(Z)][1/(1+F)]$, where χ refers to the charge (spin) susceptibility for $F = F^{S(A)}$ and analogously for all the other orbital and spin-orbital ($G^{S(A)}$ and $H^{S(A)}$ parameters) susceptibilities. By calculating in DMFT the quasiparticle residue Z

and all six susceptibilities, we obtain the F parameters of the model as a function of U/W .

Figure 2 shows the decrease of Z in the metallic solution on approaching the MIT. Superconductivity sets in at $Z = Z_{\text{crit}} \cong 0.06$, a very small value indeed. The charge compressibility decreases as a function of U/W and vanishes at the MIT, consistent with the approaching incompressible insulator. The spin and all four orbital and spin-orbital susceptibilities, which initially increase at small U/W (Stoner enhancement), turn around at $U/W \sim 0.7$, eventually vanishing at the MIT, consistent with a spin and orbital gap in the insulator. Accordingly, F^S monotonically increases from $\sim U/W$ at weak coupling to infinity at the MIT, whereas the other parameters F^A , $G^{S(A)}$, and $H^{S(A)}$ start off negative proportional to $-U/W$ roughly until $U \sim ZW$, but then turn upward, cross zero, and finally diverge like $1/Z^2$ at the MIT.

This behavior of the Landau parameters in the metallic phase is at the root of the superconducting instability, as is seen by calculating the quasiparticle pair s -wave scattering amplitude A . A has two contributions, $A_{i \rightarrow i}$ and $A_{i \rightarrow j}$, describing singlet pair scattering from orbital i into the same or into another orbital, respectively. They are given by $A_{i \rightarrow i} = [(Z)/(12\rho_0)] [(F^S)/(1 + F^S)] - 3[(F^A)/(1 + F^A)] + 2[(G^S)/(1 + G^S)] - 6[(G^A)/(1 + G^A)]$, and $A_{i \rightarrow j} = [(Z)/(8\rho_0)] (-[(H^S)/(1 + H^S)] + 3[(H^A)/(1 + H^A)] + [(G^S)/(1 + G^S)] - 3[(G^A)/(1 + G^A)]$. Figure 2 shows the pair amplitude $A = A_{i \rightarrow i} + 2A_{i \rightarrow j}$. At weak coupling, $A_{i \rightarrow i} = U + 4J_H/3 > 0$ and $A_{i \rightarrow j} = J_H$, so that $A = U + 10J_H/3$ is repulsive. However, as the MIT is approached and all F parameters diverge, $A \rightarrow -Z/2\rho_0$, attractive and about equal to half of the quasiparticle bandwidth $W_*/2 = ZW/2$, confirming

our proposed scenario. In fact, the assumption of a quasiparticle repulsion renormalized by Z (12) and an unrenormalized attraction J_H would imply here $A \cong ZU + 10J_H/3$. This simple expression is seen to compare remarkably well with the true A up to $(U/W)_c$, leading to a very accurate estimate of 0.067 for Z_{crit} .

The crossover from weak to strong correlations occurs when the lower and upper Hubbard bands separate from each other, uncovering the quasiparticle resonance in the spectral function. This suggests a two-component description of the model, similar to that used to analyze the MIT in terms of the Kondo effect (13). We find that a two-component model describes very well the strongly correlated superconducting phase, in particular the probability $P(n)$ for a site to possess n electrons in the ground state. We calculated $P(n)$ (the total weight of sites with occupancy n in the ground state) for the superconductor (Fig. 3, B to D) and that for the nearby Mott insulator $P_{\text{ins}}(n)$ (Fig. 3A) to find that they are quite similar. In spite of an exceedingly large Δ , there is no evidence of preformed pairs or bipolarons in the superconductor, as underlined by the strong steady peaking of $P(n)$ around $n = 2$.

By assuming the "two-component" form $P(n) = ZP_{\text{qp}}^{(\text{SC})}(n) + (1 - Z)P_{\text{ins}}(n)$, where Z , $P(n)$, and $P_{\text{ins}}(n)$ are known, we extracted the quasiparticle probability distribution $P_{\text{qp}}^{(\text{SC})}$ in the strongly correlated superconductor between $U/W = 0.8$ and $U/W = 0.9$ (Fig. 3, A' to D'). It shows strong oscillations between even and odd n , as expected for a superconductor, with no major variations as a function of U/W even close to the Mott tran-

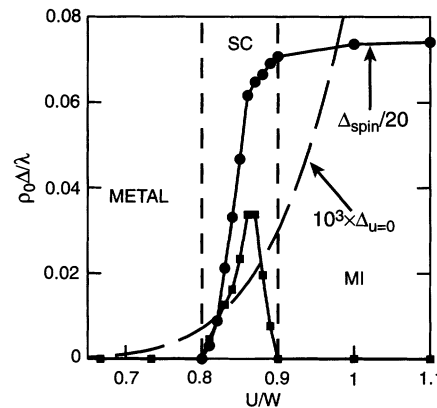


Fig. 1. Superconducting gap Δ (squares) as a function of $U/W \equiv 50|J_H|/W$. SC and MI stand for superconductor and Mott insulator, respectively. Also shown are the spin gap Δ_{spin} , reduced by a factor of 20 (circles), and the BCS gap calculated as a function of $50|J_H|/W$ at $U = 0$ and multiplied by 1000 (long-dashed line). Gaps are normalized to $\lambda/\rho_0 = 10|J_H|/3$, which measures the pair attraction.

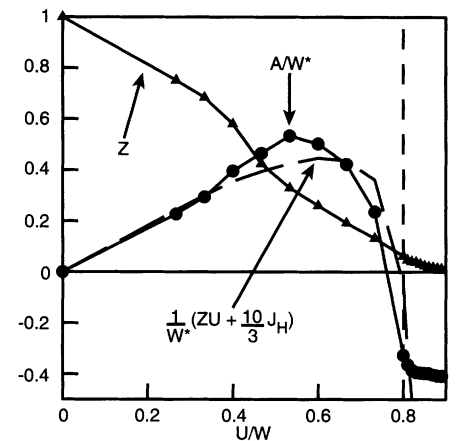


Fig. 2. Quasiparticle residue Z (triangles) as function of U/W . The vertical dashed line at $U/W = 0.8$ identifies the critical value above which the metallic solution may spontaneously develop a superconducting order parameter. The quasiparticle scattering amplitude A (circles) and its heuristic approximation $ZU + 10J_H/3$ (long-dashed line) are also shown, both crossing zero at the metal-superconductor transition.

sition ($U/W = 0.9$), which is consistent with a weak to intermediate coupling superconductivity, implied by $A \equiv -W_*$. As a check, $P_{qp}^{(METAL)}(n)$ in the (metastable) nonsuperconducting metal is also extracted (Fig. 3, A'' to C'') and found to be similar to that of a free Fermi liquid (Fig. 3D''), indicating almost free quasiparticles. The accuracy shown by this check is remarkable, as $P_{qp}^{(METAL)}$ is but a tiny fraction $\sim Z$ of $P(n)$ and there is no free parameter. We conclude that, in the strongly correlated superconductor, free fermion-like quasiparticles of weight Z become strongly paired while floating in a prevailing Mott insulator background. That background slows them down while taking away their Coulomb repulsion, but not their onsite (here Jahn-Teller-originated) pair attraction. Somewhat similar to systems with spin-charge separation, the charge degrees of freedom are strongly renormalized close to the Mott transition, but the spin degrees of freedom (here including the pairing attraction) are not. The phase diagram of Fig. 1 for increasing U bears a remarkable similarity to that of cuprates for decreasing doping. We believe the superconductivity in the $t - J$ model of cuprates to be in fact of a deeply similar origin, although the intersite antiferromagnetic interaction does of course introduce important differences over our onsite J_H . The mechanism inducing singlet formation without competition with the Coulomb repulsion U is not far in spirit from Anderson's original RVB idea for cuprates (7).

Coming to fullerenes, we are only beginning to explore the full phase diagram and calculate T_c and other properties for variable electron and hole doping. The possibility that

superconductivity in these systems could be of the present strongly correlated kind seems real. Even if our solution is obtained for $\langle n \rangle = 2$ or 4 (where superconductivity has not yet been found), whereas the investigation of the $\langle n \rangle = 3$ case (where superconductivity is actually observed) requires further work, we expect a very similar scenario for the latter case as well. In particular, the chemically expanded $\langle n \rangle = 3$ system of $(NH_3)K_3C_{60}$ is experimentally found to be insulating with low spin ($S = 1/2$), rather than high spin ($S = 3/2$), as expected for a regular Mott state (14). The low spin is clearly of Jahn-Teller origin, indicating a Mott-Jahn-Teller insulator, exactly as in the $\langle n \rangle = 4$ case of K_4C_{60} .

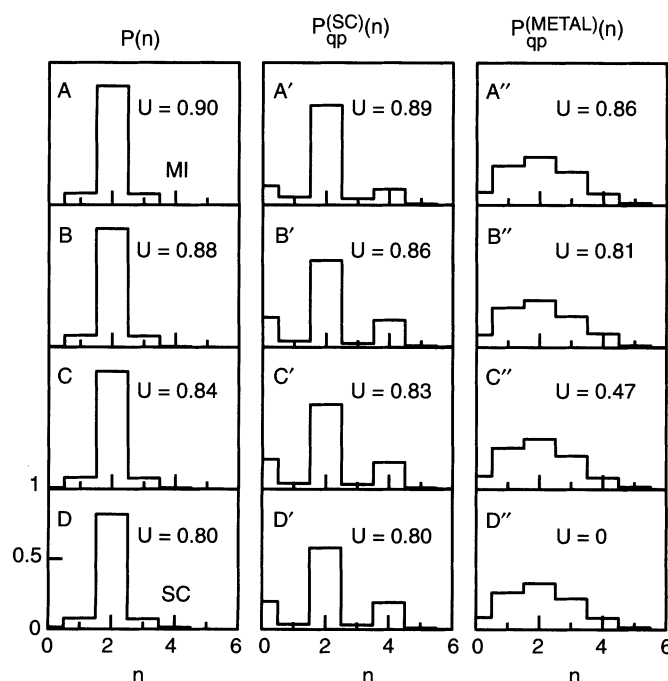
An important detail in fullerenes is the actual value of the superconducting λ . Strict electron-phonon coupling would yield a realistic value of $\lambda \sim 0.8$ to 1.1 (3). If alone, this large coupling would place fullerene superconductors in the intermediate coupling regime already at $U = 0$. There, a further increase of λ should not really raise much T_c or might even reduce it, in contrast with the well-known strong increase of T_c with increasing volume (15). An independent estimate of the effective pair attraction can be obtained by comparing the spin gap observed both in insulating K_4C_{60} (16) and in superconducting K_3C_{60} (17) $\Delta_{spin} \approx 0.07$ to 0.1 eV with that of our $J_H < 0$ model, through $\Delta_{spin} \approx 5|J_H|$ (18). We get in this way $J_H \approx -0.02$ eV $\approx -0.02 U$, hence $\lambda \approx 0.13$, which is the tentative value adopted here. This large reduction of the effective λ must, as explained above, be due to strong cancellation by the bare Hund's rule $J_H \sim 0.05$ eV (19).

With a reduced λ and large U , the only way to explain superconductivity and its increasing T_c with volume (increasing U/W) is to invoke the strongly correlated superconductivity we found just above $(U/W)_c$. For further volume expansion, our model predicts, as in Fig. 1, an eventual decline of T_c and a Mott insulator for integer filling. Both features are observed in ammoniated compounds of the K_3C_{60} family (20). In the K_4C_{60} family, conversely, U/W is above the MIT value, and we have Mott-Jahn-Teller insulators. Finally, we surmise that a similar strongly correlated superconductivity, modified to account for the $d = 5$ degeneracy of the h_u hole states, should be relevant to the recently discovered $C_{60}(n+)$ superconductivity (21). Here a somewhat stronger electron-phonon coupling has been observed (21) and calculated (2), whereas the hole bandwidth and intramolecular Coulomb repulsion are most likely similar to those of electrons. The enhanced superconductivity in $C_{60}CHCl_3$ and $C_{60}CHBr_3$ expanded lattices could result from the increase of U/W and of electronic correlations, whereas the alternative explanation of a BCS-like increase in the density of states has been put in deep question by very recent results (22). The full development of the theory of $C_{60}(n+)$ superconductivity is a task we reserve for the near future.

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Fig. 3. Occupation probabilities for the particles, $P(n)$, and for the quasiparticles in the superconducting and in the metallic phases, $P_{qp}^{(SC)}(n)$ and $P_{qp}^{(METAL)}(n)$, respectively.



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