Statistical properties of the spin liquid: Interpretation of the hole states and exchange-mediated pairing

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The metallic phase of strongly correlated electrons is discussed within a novel statistical approach that correctly reproduces the principal features of the Mott insulating state when localization is reached at half-filled band ($n=1$). The entropy in the normal phase decomposes into a spinless-fermion part representing holes, and a part describing moments. The explicit form of the superconducting gap $\Delta_{\mathbf{k}}$ is derived; this solution is shown to disappear when $n=1$. Most of the results cannot be obtained by using the Fermi-Dirac distribution for single-particle states.

We have recently proposed[1,2] a novel approach to strongly correlated metals (*spin liquids*) at temperature $T>0$. This approach properly describes the transformation of correlated itinerant states into a lattice of localized spins when the Mott insulator limit is reached (band filling $n\rightarrow 1$). The treatment is based on the fundamental observation that when the magnitude U of the short-range Coulomb interaction[3] far exceeds the renormalized band energy per particle, the doubly occupied singlet-spin configurations $|i\uparrow\downarrow\rangle$ must be excluded not only in the real-space (Wannier, $\mathbf{R}_i$) representation but also in the reciprocal-space (Bloch, $|\mathbf{k}\rangle$) basis. This concept of projected fermion states in $\mathbf{k}$ space has been applied subsequently to the resonating-valence-bond (RVB) state[4] and the superconductivity.[5]

In this paper, we explicitly describe several basic properties of such electron liquid. The novel findings are as follows: First, we show that the holes in the Mott insulator (or more precisely in the lowest Hubbard subband[3]) may be regarded as *spinless fermions*. Second, we prove that the newly proposed[1] distribution function for quasiparticles removes the redundancy of the number of states for the half-filled case obtained with the fermion representation in the Gutzwiller ansatz[6,7] for strongly correlated electrons. The limiting case of the Mott insulator is correctly described only if the redundancy is removed. To achieve these results we characterize the normal phase by the distribution of single-particle energies $\{E_{\mathbf{k}}\}$ in the $U\rightarrow\infty$ limit. In this respect, our approach represents a *quasiclassical* statistical description of the normal and metallic RVB state[4] in the $U\rightarrow\infty$ limit, since we disregard quantum pair spin-flip processes characteristic for this state when U is large but finite. Third, we include exchange-mediated singlet-pairing and in the mean-field approximation obtain the superconducting gap $\Delta_{\mathbf{k}}$ when both two- and three-site pairing parts are included. Finally, we show that the superconductivity (SC) disappears when $n\rightarrow 1$; we thus eliminate the spurious solution obtained when the Fermi-Dirac (FD) distribution is used to describe quasiparticle states.

To emphasize from the outset the difference between the properties of the spin liquid (SL) and the ordinary Fermi liquid (FL) we have plotted in Figs. 1 and 2 the distribution function as a function of particle energy ε, and the entropy S for $T\rightarrow\infty$ as a function of n, respectively. The position of the chemical potential μ differs for those two systems.[1] Moreover, the total occupancy $\bar{n}_{\mathbf{k}}=\bar{n}_{\mathbf{k}\uparrow}+\bar{n}_{\mathbf{k}\downarrow}$ has been plotted for the SL case and compared with $\bar{n}_{\mathbf{k}\uparrow}=\bar{n}_{\mathbf{k}\downarrow}=\bar{n}_{\mathbf{k}}/2$ for the FL case. The difference in the values of S as $n\rightarrow 1$ arises because both the empty $|\mathbf{k}0\rangle$, and the doubly occupied $|\mathbf{k}\uparrow\downarrow\rangle$ states are excluded for the SL state; they are retained in the FL case.[8] Only the former (SL) model correctly reproduces the entropy of the Mott insulator.[1] This model is shown to provide a coherent theory for $n<1$ as well.

To analyze the physical consequences of the new approach[1,2] we consider first the normal state in the absence of magnetic field, for which the distribution function in $U\rightarrow\infty$ limit is

$$\bar{n}_{\mathbf{k}\sigma}=\tfrac{1}{2}\{1+\tfrac{1}{2}\exp[\beta(\varepsilon_{\mathbf{k}}-\mu)]\}^{-1}\equiv f_{\mathbf{k}}, \tag{1}$$

with $\beta\equiv(k_BT)^{-1}$. This may be rewritten as

$$\bar{n}_{\mathbf{k}\sigma}=\tfrac{1}{2}\{1+\exp[\beta(\varepsilon_{\mathbf{k}}-\bar{\mu})]\}^{-1}\equiv\tfrac{1}{2}\bar{f}_{\mathbf{k}}, \tag{2}$$

where $\bar{\mu}\equiv\mu+k_BT\ln 2$, and $\bar{f}_{\mathbf{k}}$ is the FD function with the shifted chemical potential $\bar{\mu}$. The distribution (1) is obtained in the standard manner[1] or by defining projected particle-number operator $\tilde{n}_{\mathbf{k}\sigma}\equiv a^{\dagger}_{\mathbf{k}\sigma}a_{\mathbf{k}\sigma}(1-a^{\dagger}_{\mathbf{k}-\sigma}a_{\mathbf{k}-\sigma})$, where $a^{\dagger}$ and a are fermion operators, and are calculating the expectation value $\bar{n}_{\mathbf{k}\sigma}$ within the grand ensemble formalism.

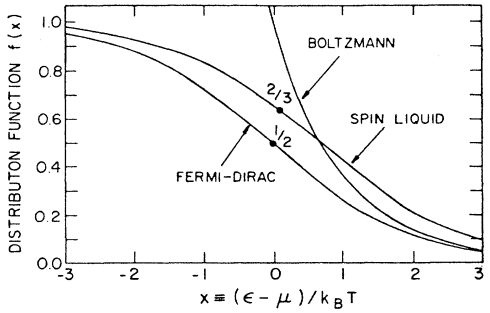

FIG. 1. The comparison of the energy dependence of the distribution function for the spin liquid (for $\bar{n}_{\mathbf{k}}$) with those for the Fermi-Dirac (for $\bar{n}_{\mathbf{k}\sigma}$) and Boltzmann distributions.

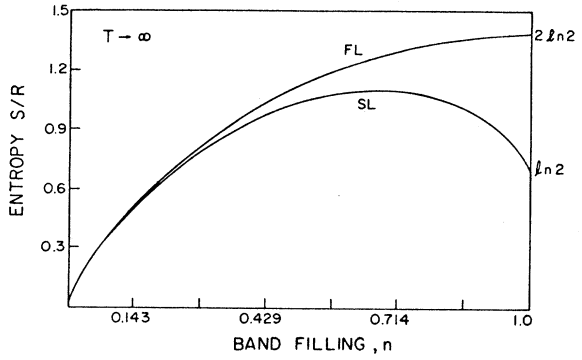

FIG. 2. The limiting ($T\rightarrow\infty$) value of the entropy (per site) vs band filling n for the FL and SL states. The constant $R\equiv k_BN$.

Using Eq. (2), one obtains the internal energy $E(T)=(1/N)\sum_{\mathbf{k}}\varepsilon_{\mathbf{k}}\bar{f}_{\mathbf{k}}$ and the shifted chemical potential $\bar{\mu}$ throughout the relation $n=(1/N)\sum_{\mathbf{k}}\bar{f}_{\mathbf{k}}$. These expressions for nN spinless fermions with $\mu=\bar{\mu}$, can be transformed to the following integral forms

$$E(T)=\int_{-W/2}^{W/2}E\rho(E)\bar{f}(E)dE\,, \tag{3}$$

and

$$n=\int_{-W/2}^{W/2}\rho(E)\bar{f}(E)dE\,, \tag{4}$$

where $\rho(E)$ is the density of states (DOS) per site per spin, and W is the particle bandwidth. Equations (3) and (4) are of the same form as for fermions but with the customary factor of 2 missing, i.e., as if only half of the total DOS had been taken. This halving reflects the splitting of the underlying bare band into two Hubbard subbands.[3]

The integrals in (3) and (4) may be explicitly evaluated for a featureless form of $\rho(\varepsilon)$; we obtain

$$\mu=-k_BT\ln 2+k_BT\ln\frac{\exp(n\beta W)-1}{1-\exp[(n-1)\beta W]}-\frac{W}{2}\,. \tag{5}$$

In the limit $T=0$, $\mu=W(n-\frac{1}{2})$, which for $n=1$ leads to $\mu=W/2$, i.e., the band is full. This fact proves *directly* that the number of states in the band and with distribution function (1) or (2) is N, not $2N$ (as for ordinary fermions.) Thus, the redundant states appearing in the Gutzwiller approximation[6,7] in the limit $n\rightarrow 1$ have been automatically removed in the present approach. Also, in the limit $T=0$ Eq. (3) [with μ given by (5)] reduces to

$$E(T=0)=-(W/2)n(1-n)\,, \tag{6}$$

which coincides with that obtained within the Gutzwiller ansatz[6,9] in the limit $U/W\rightarrow\infty$. Thus, the scaling factor $(1-n)$ renormalizing the band energy[6,7,9] also appears automatically in the present approach.

Next, consider the normal state in applied magnetic field H_a. The general expression for the entropy is then[1]

$$S_L=-k_B\sum_{\mathbf{k}}\left[(1-\bar{n}_{\mathbf{k}})\ln(1-\bar{n}_{\mathbf{k}})+\sum_{\sigma}\bar{n}_{\mathbf{k}\sigma}\ln\bar{n}_{\mathbf{k}\sigma}\right]. \tag{7}$$

By introducing magnetic moment $\bar{m}_{\mathbf{k}}$ per particle through the relation

$$\bar{m}_{\mathbf{k}}=(\bar{n}_{\mathbf{k}\uparrow}-\bar{n}_{\mathbf{k}\downarrow})/(\bar{n}_{\mathbf{k}\uparrow}+\bar{n}_{\mathbf{k}\downarrow})\,, \tag{8}$$

we obtain the following expression for the entropy

$$S_L=-k_B\sum_{\mathbf{k}}[(1-\bar{n}_{\mathbf{k}})\ln(1-\bar{n}_{\mathbf{k}})+\bar{n}_{\mathbf{k}}\ln\bar{n}_{\mathbf{k}}+\bar{n}_{\mathbf{k}}\left[\frac{1-\bar{m}_{\mathbf{k}}}{2}\ln\frac{1-\bar{m}_{\mathbf{k}}}{2}+\frac{1+\bar{m}_{\mathbf{k}}}{2}\ln\frac{1+\bar{m}_{\mathbf{k}}}{2}\right]]\,. \tag{9}$$

The first two terms represent the entropy of spinless fermions, associated with holes in the lower subband.[10] The last two terms represent the entropy of magnetic moments weighted with the probability that the given state is occupied. In the limit $\bar{n}_k\rightarrow 1$ this part reduces to the usual entropy of a magnetized system of spins $s=\frac{1}{2}$, which represents a *necessary condition* to be fulfilled by any theory claiming to properly describe the situation in the Mott insulator limit.

For $H_a\neq 0$, the method of most probable distribution[1] as applied to (7) leads to the distribution

$$\bar{n}_{\mathbf{k}\sigma}=(1-\bar{n}_{\mathbf{k}-\sigma})\{1+\exp[\beta(\varepsilon_{\mathbf{k}\sigma}-\mu)]\}^{-1}\,. \tag{10}$$

Application of this distribution in the mean-field approximation provides the following equation for the magnetic moment $m=\langle n_{i\uparrow}-n_{i\downarrow}\rangle$ per site

$$m=n\tanh\left(\frac{\mu_BH_a-Jzm}{k_BT}\right), \tag{11}$$

which holds for an arbitrary DOS. In this equation J is the magnitude of the kinetic exchange interaction which is present for the strongly correlated electrons,[11] and z is the number of nearest neighbors. Here we have used condition (5) for μ when $H_a\neq 0$. We see that the magnetic polarization of the spin liquid follows the magnetization curve of nN localized spins. This situation arises because the double occupancies are suppressed; hence, unlike the case of the Pauli paramagnet, no reduction of m occurs due to the spin pairing below the Fermi level. The form (11) will lead to the Curie-Weiss law for the static susceptibility $[\chi\sim(T+\theta)^{-1}]$ in the normal phase. If θ is large (>1000 K) then the susceptibility will be small and almost flat, as observed in almost all high-T_c systems.

Next, we use the projected fermions in $\mathbf{k}$ space explicitly when considering a condensed Bardeen-Cooper-Schrieffer (BCS) type of state within the exchange-mediated high-T_c superconductivity.[12] The effective Hamiltonian with a full pairing part (i.e., with the three-site terms) in real space derived before[13] is

$$\tilde{\mathcal{H}}=\sum_{ij\sigma}t_{ij}b_{i\sigma}^{\dagger}b_{j\sigma}-\sum_{ijk}(2t_{ij}t_{jk}/U)b_{ij}^{\dagger}b_{kj}\,, \tag{12}$$

where t_{ij} is the hopping integral, U is the magnitude of the Coulomb interaction, and $b_{i\sigma}^{\dagger}\equiv a_{i\sigma}^{\dagger}(1-n_{i-\sigma})$ and $b_{ij}^{\dagger}\equiv(1/\sqrt{2})(b_{i\uparrow}^{\dagger}b_{j\downarrow}^{\dagger}-b_{i\downarrow}^{\dagger}b_{j\uparrow}^{\dagger})$ are, respectively, the projected single-particle and pairing operators; the projections arise from exclusion of site double occupancies *in real space*. Inclusion of both two-site ($i=k$) and three-site ($i\neq k$) terms in (12) leads to important consequences.

First, transform (12) into the **k** space

$$\tilde{\mathcal{H}} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} b^{\dagger}_{\mathbf{k}\sigma} b_{\mathbf{k}\sigma} - (2/UN) \sum_{\mathbf{k}\mathbf{k}'\mathbf{q}} \varepsilon_{\mathbf{k}-\mathbf{q}/2} \varepsilon_{\mathbf{k}'-\mathbf{q}/2} b^{\dagger}_{\mathbf{k}+\mathbf{q}/2,-\mathbf{k}+\mathbf{q}/2} \times b_{\mathbf{k}'+\mathbf{q}/2,-\mathbf{k}'+\mathbf{q}/2}, \quad (13)$$

where

$$b^{\dagger}_{\mathbf{k},\mathbf{k}'} = (1/\sqrt{2})(b^{\dagger}_{\mathbf{k}\uparrow} b^{\dagger}_{\mathbf{k}'\downarrow} - b^{\dagger}_{\mathbf{k}\downarrow} b^{\dagger}_{\mathbf{k}'\uparrow}),$$

and $\varepsilon_{\mathbf{k}}$ and $b^{\dagger}_{\mathbf{k}\sigma}$ are the space-Fourier transforms of t_{ij} and $b^{\dagger}_{i\sigma}$, respectively. Unfortunately, the operators $b^{\dagger}_{\mathbf{k}\sigma}$ and $b_{\mathbf{k}\sigma}$ do not anticommute to a number because we used projected operators. This difficulty may be overcome by limiting ourselves to the classes of projected wave functions which fulfill the identity

$$|\Phi_0\rangle \equiv \prod_{\mathbf{k}} (1 - n_{\mathbf{k}\uparrow} n_{\mathbf{k}\downarrow}) |\Phi_0\rangle . \quad (14)$$

The above property of the projected wave function is automatically preserved by introducing *projected fermion operators* $\tilde{a}^{\dagger}_{\mathbf{k}\sigma} \equiv a^{\dagger}_{\mathbf{k}\sigma}(1 - n_{\mathbf{k}-\sigma})$ and $\tilde{a}_{\mathbf{k}\sigma} \equiv a_{\mathbf{k}\sigma}(1 - n_{\mathbf{k}-\sigma})$, respectively.[1] Such projection is analogous to that proposed before[9,10] in the real-space representation. Then, $\tilde{n}_{\mathbf{k}\sigma} = \tilde{a}^{\dagger}_{\mathbf{k}\sigma}\tilde{a}_{\mathbf{k}\sigma} = n_{\mathbf{k}\sigma}(1 - n_{\mathbf{k}-\sigma})$, and the starting condition that $\tilde{n}_{\mathbf{k}\uparrow} + \tilde{n}_{\mathbf{k}\downarrow} = 0$ or 1 is obeyed automatically. The new operators still have *nonfermion anticommutation relations* but the reformulation of the problem in this new form renders the solution of $\tilde{\mathcal{H}}$ tractable, at least in the mean-field approximation.

Namely, the Hamiltonian (13) is solved by choosing the trial wave function of the BCS form in the projected fermion-operator representation

$$|\Phi\rangle = \prod_{\mathbf{k}} (u_{\mathbf{k}} + v_{\mathbf{k}} \tilde{a}^{\dagger}_{\mathbf{k}\uparrow} \tilde{a}^{\dagger}_{-\mathbf{k}\downarrow}) |\Phi_0\rangle .$$

Within the class of wave function fulfilling the condition (14) we can rewrite (13) in the form[14]

$$\tilde{\mathcal{H}} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} \tilde{a}^{\dagger}_{\mathbf{k}\sigma} \tilde{a}_{\mathbf{k}\sigma} - (4/UN) \sum_{\mathbf{k}\mathbf{k}'} \varepsilon_{\mathbf{k}} \varepsilon_{\mathbf{k}'} \tilde{a}^{\dagger}_{\mathbf{k}\uparrow} \tilde{a}^{\dagger}_{-\mathbf{k}\downarrow} \tilde{a}_{-\mathbf{k}'\downarrow} \tilde{a}_{\mathbf{k}'\uparrow} . \quad (15)$$

Thus, the inclusion of the three-site terms leads to a *separable* **k**-dependent singlet-spin pairing potential $V_{\mathbf{k}\mathbf{k}'} = -4\varepsilon_{\mathbf{k}}\varepsilon_{\mathbf{k}'}/UN$. Furthermore, one sees that (15) corresponds to (13) if only terms with $\mathbf{q} = 0$ are included in the second term and if we replace the operators $b_{\mathbf{k}\sigma}$ by the projected operators $\tilde{a}_{\mathbf{k}\sigma}$. In other words, our approximation scheme is complementary to the Gutzwiller scheme[6,7] which is based on the removal of double occupancies in the real space. Yet, the present approach leads to the results which are in some aspects similar, as discussed above. This may mean that both the Gutzwiller and the present formulations of the correlated state contain some universal features, the validity of which goes beyond the approximation scheme involved.

For the choice (14) of $|\Phi_0\rangle$, the distribution (1) should be used instead of the FD function. Then, the superconducting gap equation is of the type

$$\Delta_{\mathbf{k}} = -\frac{4\varepsilon_{\mathbf{k}}}{UN} \sum_{\mathbf{k}'} \frac{\varepsilon_{\mathbf{k}'}\Delta_{\mathbf{k}'}}{2\tilde{E}_{\mathbf{k}}} (1 - 2f_{\mathbf{k}'}) , \quad (16)$$

where $f_{\mathbf{k}}$ is given by Eq. (1), and $\tilde{E}_{\mathbf{k}} = [(\varepsilon_{\mathbf{k}} - \mu)^2 + |\Delta_{\mathbf{k}}|^2]^{1/2}$ is the energy of quasiparticles in the SC phase. A very important conclusion following from (16) is that the **k** *dependence (and symmetry) of* $\Delta_{\mathbf{k}}$ *is the same as that for* $\varepsilon_{\mathbf{k}}$. In the case of high-T_c superconductors modeled by a planar configuration of Cu and O atoms with $\varepsilon_{\mathbf{k}} = zt[\cos(k_x a) + \cos(k_y a)]$, the solution is of an extended s-wave form, independent of the type of the distribution function or of the DOS form (the same result is obtained for the mean-field solution with Gutzwiller ansatz if the full $V_{\mathbf{k}\mathbf{k}'}$ is taken). So, contrary to earlier approaches, $\Delta_{\mathbf{k}} \sim \varepsilon_{\mathbf{k}}$ can now be explicitly specified.

Writing $\Delta_{\mathbf{k}} = \Delta(T)\varepsilon_{\mathbf{k}}$ we obtain from (16) either that $\Delta \equiv 0$ or $\Delta \neq 0$ obeys the equation

$$1 = \frac{4}{UN} \sum_{\mathbf{k}} \frac{\varepsilon_{\mathbf{k}}^2}{2\tilde{E}_{\mathbf{k}}} (1 - 2f_{\mathbf{k}}) . \quad (17)$$

This equation must be supplemented with the equation specifying μ:

$$1 - n = \frac{1}{N} \sum_{\mathbf{k}} \frac{|\varepsilon_{\mathbf{k}} - \mu|}{\tilde{E}_{\mathbf{k}}} (1 - 2f_{\mathbf{k}}) = \frac{1}{N} \sum_{\mathbf{k}} \frac{|\varepsilon_{\mathbf{k}} - \mu|}{\tilde{E}_{\mathbf{k}}(1 + 2e^{-\beta\tilde{E}_{\mathbf{k}}})} . \quad (18)$$

If the FD function is taken for $f_{\mathbf{k}}$, then Eq. (17) differs from the standard BCS result by the factor $\varepsilon_{\mathbf{k}}^2$ in the numerator, and by the fact that $|\Delta_{\mathbf{k}}|^2 = |\Delta|^2 \varepsilon_{\mathbf{k}}^2$. For the SL state the form (1) should be introduced and this leads to two new important features. First, since the particle levels are singly occupied and the exchange interaction takes place between all electrons, the summation in (17) should be taken over the *whole* Brillouin zone, and not be limited to states close to μ. Second, in the limit of the Mott insulator (i.e., for $n \rightarrow 1$) no superconducting solution with $\Delta \neq 0$ exists; this result is again not limited to a particular form of DOS. To prove this statement one notices that Eq. (18) then yields $2f_{\mathbf{k}} \equiv 1$. This form of $f_{\mathbf{k}}$, corresponding to the filled Hubbard subband state, when substituted in (17) leads to a contradiction. Hence, the $\Delta \equiv 0$ solution must be chosen. In other words, the T_c *vanishes as* $n \rightarrow 1$. Thus, with the new statistics one avoids the spurious solution obtained with $\Delta \neq 0$, which is inherent in the standard mean-field approximation.[12,13] Also, it does not necessitate a decomposition into holon and spinon parts of the pairing interaction,[15] though the result is the same in both formulations.

In summary, we have discussed the statistical properties of strongly correlated electron systems (*the spin liquid*), using a novel approach[1] based on exclusion of double occupancies in **k** space. The entropy can be decomposed into the spinless-fermion and the localized-moment parts. The existence of the well-defined magnetic moments within this approach does not preclude superconductivity because the latter is due to mutual spin-singlet pairing induced by antiferromagnetic exchange interactions. We have also shown that if the full pairing part (with the three-site terms) is included, then the mean-field (BCS-type) solution automatically leads to a **k** dependence of superconducting gap, $\Delta_{\mathbf{k}} = \Delta\varepsilon_{\mathbf{k}}$. The superconductivity vanishes in the Mott-insulator limit. These results prove the usefulness of the concept of the spin liquid developed here and in Ref. 1. The detailed numerical analysis of the superconducting and antiferromagnetic phases requires a separate treatment.

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