Phase Separation and Superconductivity in the Copper-Oxide Chain.

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Abstract. - The phase diagram of the copper-oxide chain as a function of density and the nearest-neighbour Coulomb interaction, \( V \), is determined. Phase separation takes place above a critical value of \( V \) when the Cu\(^{2+} \) → Cu\(^{+} \) valence fluctuations dominate. In the proximity of the phase separation boundary the superconducting correlations are the most divergent. We identify the parameter regions where the Luttinger-liquid theory applies and calculate the contours of the charge-charge correlation exponent \( K_\sigma \). We show that anomalous flux quantization occurs as \( K_\sigma \) diverges. At \( n = 1 \), for \( V > t \), a gap opens in the spectrum and the ground state is a charge density wave.

The high-temperature superconductors are difficult to understand quantitatively because of the failure of mean-field theories and perturbation methods to give reliable results both in reduced dimensions and in the presence of strong electronic interactions. Under these circumstances exact calculations of finite-size systems can provide valuable information. In particular, the results of Luttinger-liquid theory enable thermodynamic correlation functions to be deduced for one-dimensional systems via exact calculations on finite-size chains. In this letter we solve exactly finite-length copper-oxide chains, up to a maximum of 12 sites, using the Lanczos procedure with the anticipation that the copper-oxygen Coulomb repulsion. We identify the phase separation boundary of the extended Hubbard model via a Maxwell construction. Then we identify the region of possible superconductivity using the results of Luttinger-liquid theory and by the onset of anomalous flux quantization.

Our model for the copper-oxide chain consists of two atoms per unit cell. By neglecting the

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oxygen-oxygen hybridization and considering the Coulomb interaction up to first nearest neighbours, the copper-oxide chain is described by the two-band model Hamiltonian,

\[ H = H_t + \frac{\Delta}{2} \sum_{ij} (p_{ij}^+ p_{ij} - d_{ij}^+ d_{ij}) + U_d \sum_i d_{i\uparrow}^+ d_{i\uparrow} d_{i\uparrow}^+ d_{i\uparrow} + U_p \sum_j p_{j\uparrow}^+ p_{j\uparrow} p_{j\uparrow}^+ p_{j\uparrow} + V \sum_{\langle ij \rangle \sigma} (d_{iz\sigma}^+ d_{iz\sigma} p_{jz\sigma}^+ p_{jz\sigma}) + \left( \frac{U_d + U_p}{4} + 2V \right) (N_s - N_p), \]

where

\[ H_t = -t \sum_{\langle ij \rangle \sigma} (d_{iz\sigma}^+ p_{jz\sigma} + \text{h.c.)}. \]

i and j are copper and oxygen sites, respectively, \( \langle ij \rangle \) represents nearest neighbours and the operator \( d_{iz\sigma}^+ \) creates a Cu (O) hole with spin \( \sigma \). \( \Delta \) is the charge transfer energy, \( U_d \) (\( U_p \)) is the copper (oxygen) Coulomb repulsion, \( N_s \) is the number of sites, \( N_p \) is the number of particles, and \( V \) and \( t \) are the copper-oxide Coulomb repulsion and hybridization, respectively. The Hamiltonian has been defined so that it is invariant under the «particle-hole transformation» \( d_{iz\sigma}^+ \rightarrow d_{iz\sigma}, p_{jz\sigma}^+ \rightarrow p_{jz\sigma} \) and \( \Delta \rightarrow U_d - (\Delta + U_p) \), i.e. \( E(N_p, \Delta) = E(2N_s - N_p, U_d - (\Delta + U_p)) \).

In this letter we consider parameters which are chosen to fit, as far as possible, with the photoemission data of high-temperature superconductors. Thus \( U_d \sim 9t, \Delta \sim 2 - 3t \) and \( U_p \) small, where \( t \sim 1.5 \text{ eV} \) [1]. Hence the region \( 0.5 < n < 1.0 \) corresponds to \( \text{Cu}^{2+} \rightarrow \text{Cu}^+ \) valence fluctuations, while (because of the «particle-hole» symmetry of eq. (1)) the region \( 1.5 > n > 1.0 \) corresponds to \( \text{Cu}^{2+} \rightarrow \text{Cu}^{3+} \) valence fluctuations. As we are interested in the role played by the nearest-neighbour interaction, \( V \), this will be left as a free parameter.

For most regions of the phase diagram the system is metallic, for which Luttinger-liquid theory can provide a valuable insight. However, for some parameter regions in the doping range \( 0.5 < n < 1.0 \) the system is unstable with respect to phase separation. This occurs at a finite value of the nearest-neighbour Coulomb repulsion, \( V \), and we identify this phase boundary before proceeding to a discussion of the metallic regime.

Figure 1 shows the phase separation boundary as a function of \( V \) and hole density for \( U_p = 0 \) and \( U_p = t \). We set \( U_d = 9t \) and \( \Delta = 2t \); the number of sites used was 12. The boundary for this region is found using the Maxwell construction. This is given by the points \( (n_1, n_2) \) at which a tangent touches the curve of the ground-state energy vs. density. Other authors have used the point at which the compressibility, \( \kappa \), diverges (i.e. the point at which the ground-state energy vs. density becomes concave). These points, however, actually lie between \( n_1 \) and \( n_2 \) and so could be a misleading indicator for when phase separation has actually occurred. Figure 1 also shows the line of \( \kappa = \infty \). Using the Maxwell construction, the densities of the phase-separated regions are then given by \( n_1 \) and \( n_2 \), and the fraction of the system occupied by \( n_1 \) and \( n_2 \) at any given intermediate density \( n' \) is given by the relation \( m n_1 + (1 - m) n_2 = n' \), where \( m = (n_2 - n')/(n_2 - n_1) \). The tendency towards charge segregation can also be seen in the oxygen-oxygen charge correlation function [2], defined by

\[ C_{\text{edw}}(k) = \frac{1}{N_s} \sum_{\langle ij \rangle} (n_i - \langle n \rangle)(n_j - \langle n \rangle) \exp[ik(R_i - R_j)], \]

where \( n_i = \sum_{\sigma} c_{iz\sigma}^+ c_{iz\sigma} \).

The oxygen-oxygen charge correlation function (shown in fig. 2) shows a peak at \( k = \pi/3 \).
(i.e. one over the system length) for both a density of \( n = 8/12 \) and \( n = 10/12 \). This indicates a phase separation instability in the system. Phase separation occurs because, to avoid paying Coulomb repulsion, holes will tend to surround themselves with empty sites. This is because a repulsion, \( V \), between a copper and an oxygen hole actually means an attraction, \(-V\), between a copper hole and an oxygen electron. The result is that as the doping is increased away from \( n = 0.5 \), holes will tend to move onto those oxygen sites which are surrounded by empty copper sites. However, where possible, holes will stay on copper sites to avoid paying the charge transfer energy, \( \Delta \). The result is that the charge density becomes segregated and the Bloch symmetry breaks down[3].

The phase-separated region is shifted as \( U_p \) is increased into higher values of \( V \), as can be seen in the inset of fig. 1. However, the phase separation boundaries do not depend strongly on \( U_p \), provided that \( U_p < U_d - \Delta \) is satisfied.

Having determined the region of the phase diagram for which a phase separation instability occurs, we now turn our attention to the metallic phase. In the metallic region the long-distance behaviour of the correlation functions can be determined via the aid of Luttinger-liquid theory.

Luttinger liquids belong to the universality class of models described by conformal field theory with central charge, \( c = 1 \). This theory is useful because it gives relationships between the correlation exponents and a few simple properties of the finite system. Recently it has been shown that conformal field theory can be applied to models with more than one gapless excitation if the excitations are decoupled in the low-energy regime. In the low-energy regime this is true of the Hubbard model[4]. In such a case each degree of freedom has an associated operator algebra, which is again characterized by a central charge \( c = 1 \). Provided that there are no phase changes as the interactions are increased, it is reasonable to assume that Luttinger-liquid theory applies to lattice quantum models in the strong-coupling regime. In fact, this assumption can be tested \textit{a posteriori} by showing that the predictions of Luttinger-liquid theory are internally consistent. This is the assumption adopted in this paper for the extended Hubbard model.
Fig. 2. - The oxygen-oxygen charge correlation function for \( n = 10/12 \) (---) and 8/12 (---). This shows a peak at \( k = \pi/3 \) for \( V = 2t \), indicating a phase-separated state (\( U_d = 9t \), \( U_p = 0 \) and \( \Delta = 2t \)).

Fig. 3. - The Drude weight as a function of hole density for \( U_d = 9t \), \( U_p = 0 \) and \( \Delta = 2t \), showing the opening of the gap at \( n = 1 \). The copper-oxygen charge-charge correlation function for a 12-site chain at \( n = 1 \) is shown for \( V = 0.5t \) and \( 2t \). The density of electrons on the oxygen atoms rises from \( n = 1.265 \) to \( n = 1.797 \) in this range.

At long distances the charge-charge and spin-spin correlation functions are given by [5]

\[
\langle n(x) n(0) \rangle = \frac{K_x}{(\pi x)^2} + A_1 \cos(2k_f x) \frac{\ln^{-3/2}(x)}{x^{(1+K_x)}} + A_2 \cos(4k_f x) \frac{1}{x^{4K_x}}
\]

and

\[
\langle S_z(x) S_z(0) \rangle = \frac{1}{(\pi x)^2} + B_1 \cos(2k_f x) \frac{\ln^{1/2}(x)}{x^{(1+K_z)}}
\]

respectively. The superconducting correlations are similar to the spin-spin correlator with \( K_z \) being replaced by \( 1/K_z \). Hence, \( K_z \) equals 1 for free fermions with spin. \( K_z < 1 \) means that the charge and spin correlations dominate and \( K_z > 1 \) implies that the superconducting correlations are the most divergent.

Conformal field theory relates bulk quantities such as the compressibility, \( \kappa \), and the Drude weight, \( D_z \), with the charge-charge correlation exponent. Where the system behaves as a Luttinger liquid, the exponent \( K_z \) is related to the compressibility by \( K_z = (\pi/2) \kappa v_c n^2 \) and to the Drude weight by \( K_z = D_z \pi/v_c \) (where \( v_c \) is the charge velocity). These results can also be obtained from the bosonization technique; see for example ref. [5]. When analytic solutions are not available these bulk quantities [6] can be evaluated using exact diagonalization techniques [7]. The discrete compressibility is given by \( N_p^2 \kappa = 4/\left[ e(N_p + 2) + e(N_p - 2) - 2e(N_p) \right] \), where \( e(N_p) \) is the ground-state energy per site. To calculate the Drude weight the chain is
threaded with a dimensionless constant flux, $\phi$. This is done mathematically by the operator transformation, $c_{\psi} \rightarrow c_{\psi} \exp[-i\phi/N_s]$. The finite-size equivalent of the Drude weight is then $D_c = [\langle e(\phi_0 + \delta\phi) - e(\phi_0) \rangle / (2\phi^2)]$, where $\delta\phi$ is an infinitesimal flux ($\sim 0.01$) and $\phi_0$ is a background flux which removes accidental degeneracies of the ground state and guarantees a zero-current ground state. For example, $\phi_0$ is 0 (periodic boundary conditions) for $N_p = 4m + 2$ and $\pi/N_s$ (antiperiodic boundary conditions) for $N_p = 4m$ with $m$ an integer (1).

The phase diagram, fig. 1, shows the contour of $K_s = 1$, and the region for which $K_s$ exceeds 1. The expression used to calculate this contour was $K_s = \pi n \sqrt{(D_s\kappa)/2}$. Notice that for low doping $K_s$ exceeds 1 within the phase separation region given by the Maxwell construction, and as doping is increased the curve $K_s = 1$ moves out indicating that the superconducting correlations begin to dominate well within the conducting region. The points on the contour corresponding to the densities $n = 8/12$ and $n = 10/12$ are found from the 12-site chain, the point at $n = 8/10$ is found using a 10-site chain and the point at $n = 6/8$ is found using an 8-site chain. At high densities the point of $K_s$ exceeding 1 is associated with the appearance of a local minimum at $E_0(\phi_0 + \pi)$, sometimes called «anomalous flux quantization», which broadens as $V$ is increased. For the attractive Hubbard model, which is known to exhibit singlet superconductivity, the ground-state energy satisfies

$$E_0(\phi_0 + \pi) - E_0(\phi) = \frac{\Lambda}{2} \left( \frac{N_s}{\zeta} \right)^{1/2} \exp \left( -\frac{N_s}{\zeta} \right),$$

where $\zeta$ is a length associated with a gap of spin excitations and $\Lambda$ depends on details of the model [8,9]. The appearance of the minimum at $\phi_0 + \pi$ suggests the same tendency for charge pairing in the extended Hubbard model. For $n = 10/12$ and 8/10 this minimum appears just above the point at which $K_s$ exceeds 1, the result being slightly better for $n = 10/12$. The level crossings occur within the $S = 0$ subspace, indicating that singlet superconducting correlations are present.

For all other values of doping, namely $n < 0.5$ and $n > 1$, the effect of nearest-neighbour repulsion is to suppress the superconducting correlations. For the densities $n < 0.5$ and $n > 1.5$, the phase diagram rather resembles the corresponding phase diagram of the $t - U - V$ model.

Finally, we consider the effect of the nearest-neighbour repulsion at half-filling, $n = 1$. At this filling the effect of increasing $V$ is to force the system into an insulating phase. This can be seen from the graph of the Drude weight, the inset of fig. 3, which vanishes at $V \sim 1.6t$. The driving force for this change is illustrated by the charge correlation function shown in fig. 3. It shows that as $V$ is increased there is a sharp rise in the correlation function at $k = \pi$ (a wavelength of one unit cell). This corresponds to charge being pushed from copper sites onto oxygen sites, resulting in an insulating charge density wave.

In conclusion, we have established the phase diagram of the copper-oxide chain using finite cluster calculations. In the region in which $Cu^{2+} \rightarrow Cu^{+}$ charge fluctuations dominate (i.e. $\Delta \ll U_d$) we find that the coupling to the nearest-neighbour repulsion leads to a region of phase separation for a sufficiently large interaction (typically $V \sim \Delta$). In the proximity of the phase separation region and large enough density superconducting correlations are the most divergent. From our results we find that the curve $K_s = 1$ crosses the phase separation boundary at $n \sim 0.72$. At the densities $n = 8/10$ and 10/12 the divergence of $K_s$ is accompanied by anomalous flux quantization. The contour $K_s = 1$ has been calculated near

(1) For a two-band spinless Fermion model, antiperiodic boundary conditions are required at any density in order to have a zero-current ground state.
the metal-insulator transition \((n = 0.5)\) using a small number of doped holes. The trend for
the superconducting region to disappear as \(n \to 0.5\) may be a consequence of this fact. Close
to the phase separation boundary the superconducting correlations are precursory to phase
separation. At weaker coupling the role played by charge transfer excitons \([10]\) is still to be
understood.

In this one-dimensional calculation the tendency towards phase separation and
superconductivity occurs for values of \(V\) greater than the on-site oxygen repulsion \(U_p\). This
might appear to be physically unreasonable and hence invalidate this model as a theory for
high-temperature superconductors. In two dimensions, however, the effect of \(U_p\) is less
important as the dominant physical effect driving phase separation and superconductivity;
namely the avoidance of the nearest-neighbour Coulomb repulsion by oxygen holes clustering
around the same copper site \([3]\) easily operates even for large \(U_p\). This is because in two
dimensions each copper site has four neighbouring oxygen sites and oxygen holes can cluster
around the same copper site without sharing orbitals. In addition, direct oxygen-oxygen
hopping in two dimensions acts to screen \(U_p\). Hence, taking \(U_p\) small in one dimension should
give the same qualitative results as \(U_p > V\) in two dimensions.

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