Microscopic Phase Separation in the Overdoped Region of High-$T_c$ Cuprate Superconductors

Y.J. Uemura  
Department of Physics, Columbia University, New York, NY 10027, USA  
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We propose a phenomenological model for high-$T_c$ superconductors (HTSC) assuming: (1) a microscopic phase separation between superconducting and normal-metal areas in the overdoped region; and (2) existence of a homogeneous superconducting phase only below the pseudo-gap $T^*$ line, which shows a sharp reduction towards $T^* \sim 0$ at a mildly overdoped critical concentration $x_c$. This model explains anomalous doping and temperature dependences of $n_s/m^*$ (superconducting carrier density / effective mass) observed in several overdoped HTSC systems. We point out an analogy to superfluid $^3$He/$^4$He films, and discuss an energetic origin of microscopic phase separation.

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Since the discovery of high-$T_c$ cuprate superconductors (HTSC), accumulated studies have revealed unusual phenomena in the underdoped (UD) region, such as, correlations between $T_c$ and $n_s/m^*$ (superconducting carrier density / effective mass) at $T \to 0$ shown by measurements of the magnetic field penetration depth $\lambda$ [1], and the pseudo-gap phenomena [2]. These results stimulated development of various theories / models for condensation, including Bose-Einstein (BE) to BCS crossover [3,4], phase fluctuations [5,6], XY-model [7] and BE condensation [8]. These models [3-8] assume the existence of pre-formed charge pairs above $T_c$. Different pictures, however, assume single charge above $T_c$ based on the resonating-valence-bond concepts [9,10].

Several anomalous results have been found also in the overdoped (OD) region: $\mu$SR studies on Tl$_2$Ba$_2$CuO$_{6+\delta}$ (TI2201) [11,12] revealed that $n_s/m^*$ at $T \to 0$ decreases with increasing hole doping. This tendency has been observed subsequently in thin film La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) [13] and bulk YBa$_2$Cu$_3$O$_y$ (YBCO) [14] systems in the OD region. The “coherence peak” in ARPES spectra [15] also follows this behavior of $n_s/m^*$ in the OD region. Meanwhile, Tallon and Loram [16] noticed a sharp reduction of the pseudo-gap $T^*$ line in the temperature $T$ vs. hole-concentration $x$ phase diagram heading towards $T^* \sim 0$ at a critical concentration $x_c \sim 0.19$ holes/Cu which lies in the mildly OD region. In view of the existence of superconductivity in $x > x_c$ where the $T^*$ line does not exist, Tallon and Loram [16] have advocated a view point that the pseudogap phenomena is not representing pre-cursor superconducting phenomena, but should be ascribed to a tendency towards a ground state competing with superconductivity.

We have, however, suggested another possible view point in which $T^*$ is ascribed to a signature of a gradual pre-formation of pairs [4] while the anomaly in the OD region to a phase separation [4,11,17,18]. In the present paper, resorting to a model-calculation of $n_s/m^*$, comparison with experimental results, a crude estimate of competing electrostatic and condensation/pairing energies, and analogy to $^3$He/$^4$He films, we demonstrate that our picture with microscopic phase separation between superconducting and normal-metal regions can quantitatively account for several anomalous results in the OD region. We have pointed out an analogy to He films in a recent conference [18]. The present model introduces a new type of possible charge heterogeneity to HTSC systems, in addition to other known examples, such as charge/spin stripes [19].

Figure 1(a) shows the results of $T_c$ versus the muon spin relaxation rate $\sigma \propto n_s/m^*$ at $T \to 0$ of YBCO [1,14], Zn-doped YBCO ($y = 6.7$) [20] and overdoped TI2201 [11] systems. $T_c$ increases with increasing hole doping following a linear line in the UD, a saturation in the optimal region (OPT), and a recurring behavior in the OD region. This figure for HTSC systems exhibits a striking resemblance to the corresponding plot for superfluid $^3$He and $^4$He/$^3$He films in non-porous [21] and porous media [22], shown in Fig. 1(b). Here, the superfluid transition temperature $T_c$ is plotted versus the superfluid density $n_{s2d}/m^* \equiv 4n_{s2d}/m_b$ at $T \to 0$, where $n_{s2d}$ and $m_b$ represent the 2-dimensional area density and mass of superfluid He atoms (bosons) and $n_{s2d} = 2n_{s2d}$ and $m^* = m_b/2$ represent corresponding values in fermion terminology.

Simple hole doping in underdoped HTSC can be viewed as analogous to He films on Mylar [21]. Zn-doped YBCO [20] can be compared to He films in porous Yvcor glass [22], since a non-superconducting / non-superfluid area is formed around Zn / pore surface as a “healing region”, while $T_c$ is determined by the remaining superfluid density in both cases. We assumed a normal region with the area of $\pi\xi_{ab}^2$ ($\xi_{ab}$ is the in-plane coherence length) on the CuO$_2$ plane around each Zn, and showed that the reduction of $n_s/m^* (T \to 0)$ with increasing Zn concentration in YBCO and LSCO can be explained by this “swiss cheese model” [20]. This hypothesis has been confirmed by scanning tunneling microscopy (STM) measurements [23]. Such a coexistence of superfluid / normal regions can be viewed as an example of a “microscopic phase separation”. We also found a similar situation in HTSC...
superconductors with static stripe spin freezing [17].

When 3He is mixed into 4He, the superfluid transition temperature is reduced with increasing 3He fraction $p_3$, as shown by the phase diagram in the inset of Fig. 1(b). There is a large region of phase separation between boson-(3He)-rich and fermion-(3He)-rich liquids. In a bulk mixture, the lighter fermion-rich liquid in the upper part of a container does not mix with the boson-rich superfluid. Adsorption of 4He/3He mixture onto fine alumina powder [24] presumably keeps boson-rich and fermion-rich liquids coexisting in a microscopic length scale, resulting in a superfluid film in the full range of $p_3$.

The results of 4He/3He mixture on alumina powder [24] in Fig. 1(b) exhibit a roughly-linear relation between $T_c$ and the superfluid density. This behavior is analogous to that of the overdoped HTSC systems in Fig. 1(a). Both of these cases represent the response of superfluidity / superconductivity to increasing fermions (3He and holes). In all the cases of He films in Fig. 1(b), $T_c$ is determined by the area-averaged superfluid density. Similarity between Fig. 1(a) and 1(b) suggests the possibility that $T_c$ in HTSC systems may also be determined by $n_s/m^*$ at $T \to 0$ averaged over a length scale of several times $\xi_{ab}$.

Figure 2(a) compares the doping dependence of $n_s/m^*$ from $\mu$SR [11] with that of the “gapped” response $\gamma_s$ in the T-linear term $\gamma$ of the specific heat [25], observed in Ti2201. The normal state value $\gamma_n$ in Ti2201 above $T_c$ is virtually independent of doping, which implies no doping dependence of $m^* \propto \gamma$. By the broken line, we show a projected variation of the normal-state carrier density / mass, $n_n/m^* \propto x/\gamma_n \propto x$. Departure of $n_s/m^*$ from $n_n/m^*$ suggests that only a part of normal-state carriers form superfluid. We cannot ascribe this departure to the scattering effect, since the transport mean-free path $l$ of Ti2201 is much longer than $\xi_{ab}$, even for a highly overdoped sample with $T_c \sim 20$ K [26]. The BCS theory with retarded interaction cannot account for this phenomenon [4,11]. The common behavior of $n_s/m^*$ and $\gamma_s$ in Fig. 2(a) suggests a possibility that the departure of $n_s$ from $n_n$ maybe related to a volume effect.

Motivated by these observations, we propose a phase diagram of HTSC systems shown in Fig. 3, where the $T^*$ line is ascribed to pair formation, and the OD region is characterized by a phase separation between the hole-poor superconducting region with $x_f(T)$ along the $T^*$ line and the non-superconducting hole-rich region with $x_f(T)$ along the $T_c$ line in the OD region. We assume a microscopic phase separation via formation of non-superconducting regions with the length scale of $\xi_{ab}$, analogous to the “swiss cheese model” in Zn-doping, as illustrated in Fig. 3. For simplicity, we perform a model calculation assuming (1) parabolic shape of the $T_c$ line which has maximum at $T_c(x_{opt} = 0.15) = T_c^{max}$ and intersects with $x$ axis at $x_{max} = 0.27$ and $x_{min} = 0.03$; and (2) linear $T^*$ line connecting $T^*(x_{opt}) = T_c^{max}$ and $T^*(x_c = 0.19) = 0$. For a given hole concentration $x_1 \geq x_{opt}$, cooled down from high temperature, we assume the system to separate at $T \leq T_c$ into the superconducting liquid with $x_f(T)$ and normal liquid with $x_f(T)$, having the volume fraction of $p_s$ and $p_f = 1 - p_s$, respectively, where $x_1 = (x_0 p_s + x_f p_f)$. Below $T = T^*(x_1)$, the total volume becomes superfluid.

To consider an energetic origin of phase separation, let us imagine a capacitor having an area $A = \pi \xi_{ab}^2$ for $\xi_{ab} = 15$ A and thickness comparable to the average interlayer distance $c_{int} \sim 6$ A, charged with $\pm/Q \sim 2 \epsilon$ given by the deviation from average charge $(x_{max} - x_c)/2 = 0.04$ [holes/Cu] multiplied to the number of Cu atoms (48) in the area $A$. An assembly of alternating charge layers stacked along the $c$-axis direction can be expressed by sets of such capacitors with the charge $\pm/Q \sim \epsilon$ on each plate. The electrostatic energy to have one such capacitor is $E = (Q/2)^2/C \sim 0.8/\epsilon \sim 0.1 \text{ eV}$, where $\epsilon \sim 10$ represents an effective static dielectric constant due to atoms and ions between the CuO$_2$ planes, and $C$ denotes the capacitance. Imagine hole-poor and hole-rich regions, adjacent to each other, each having area $A$ on a given CuO$_2$ plane. To create this situation we need energy $2E$ per area $2A$ on a CuO$_2$ plane. In view of further energy saving via Madelung potential, we estimate the actual electrostatic energy $E_{Coulomb}$ to be roughly $\sim 0.1 \text{ eV}$.

This energy cost for charge disproportionation competes with the gain of condensation and pairing energies $E_{C_P}$ for having the hole-poor area $A$ with $q_s = A \times x_c \sim 9e$ charged paired and condensed. Assuming $\Delta = 1.7k_BT_c$ energy gain per charge and $T_c \sim 90K$, we obtain $E_{C_P} \sim 0.12 \text{ eV}$. For BE condensation, $\Delta$ should be replaced by the sum of the pairing energy $\propto k_B T^*$ and the condensation energy $\propto k_B T_c$, while for BCS condensation $E_{C_P}$ has to be multiplied by the ratio 0.1-0.2 of $\Delta$ to the effective Fermi energy $\epsilon_F \sim 0.2 \text{ eV}$. Even in the purely superconducting region at $x \leq x_c$, the system might spontaneously introduce some charge heterogeneity within $x_{min} < x < x_c$ to gain the pairing energy.

In LSCO, for example, the random spatial distribution of Sr$^{2+}$ will further reduce $E_{Coulomb}$ substantially. The area $A$ with 48 Cu atoms is associated with $N_{Sr} \sim 8$-10 Sr ions in the OPT region. We expect $\sqrt{N_{Sr}} \sim 3$ random fluctuations in this number, which would promote natural formation of hole-rich and hole-poor regions. The combination of these effects can make $E_{C_P} > E_{Coulomb}$, and possibly result in a microscopic phase separation to minimize the total energy. In the capacitor argument, both $E_{C_P}$ and $E$ are proportional to $A$. This feature does not give any preference for the magnitude of $A$. The lower limit of $A$ is related to $\xi_{ab}$ and the discreteness of the charge. The upper limit of $A$ may be related to the energy gain via $\sqrt{N_{Sr}} \propto \sqrt{A}$ and loss of percolation / proximity effect of superconducting regions for larger $A$.

Using the model shown in Fig. 3, we calculated the superfluid density $n_s(T = 0)$ as $n_s = x$ for $x \leq x_c$ and $n_s = x_c p_s$ for $x_c < x < x_{max}$, where $p_s$ and $p_f$ are volume fractions of hole-poor liquid with $x_s$ and hole-rich liquid with $x_{max}$, $p_s = 1 - p_f$, and $x = x_c p_s + x_{max} p_f$. We
assumed \( T_{\text{max}}^{\text{OD}} = 90 \, \text{K}, x_c = 0.19 \) and \( x_{\text{max}}^{\text{OD}} = 0.27 \), and show the results in the inset of Fig. 1(a). In Fig. 2(b), we also compare the published results for YBCO [14] and the variation of \( n_s \) from our calculation. The good agreements of calculation and experiments demonstrate that the phase separation can account for the “recurring” behavior of \( n_s/m^*(T \to 0) \) in the OD region and its anomalously sharp change around \( x_c \).

The \( \mu \text{SR} \) results of \( n_s/m^* \) in Tl2201 [11] and overdoped LSCO systems [27] exhibit anomalous temperature dependence characterized by increasing sharpness near \( T \sim 0 \) with increasing doping, as shown in Fig. 4(a) and 4(c). Unfortunately, the \( \mu \text{SR} \) results were obtained on ceramic specimens, which often show deviation from predicted variation for d-wave energy gap even in the OPT region. This feature prohibits detailed comparison with theories. However, we performed model calculation in the following assumptions/steps: (1) the thermal pair-breaking effect within the hole-poor superconducting region can be represented by the experimental results \( \sigma_{\text{OPT}}(T) \) obtained for specimens in the (nearly) OPT region with highest \( T_c \); (2) \( n_s/m^*(T) \) of OD specimens can be calculated by multiplying the hole concentration of the hole-poor superconducting region \( x_s(T) \) at \( T \) with its volume fraction \( p_s(T) \), and further by \( \sigma_{\text{OPT}}(T)/\sigma_{\text{OPT}}(T = 0) \). The results of this calculation, shown in Fig. 4(b) for Tl2201 and Fig. 4(c) for LSCO, reproduce the observed temperature/doping dependence very well.

In overdoped cuprates, we are not sure whether the non-superconducting hole-rich regions are spatially pinned to charge randomness, or they are dynamically fluctuating. STM measurements would be most effective to study this feature. A similar departure of \( n_s/m^* \) from \( n_n/m^* \) was also found in the 2-d organic superconductor (BEDT-TTF)\(_2\)Cu(NCS)\(_2\) [28]. It will be interesting to investigate the applicability of our model to BEDT and other superconducting systems. In conclusion, we have presented a model with microscopic phase separation to account for the anomalous behavior observed in overdoped HTSC systems. The present picture provides a possible way to reconcile the existence of superconductivity in the OD region with the sharp reduction of the \( T^* \) line.

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\[ T_{\text{max}}^{\text{OD}} = 90 \, \text{K}, \quad x_c = 0.19, \quad x_{\text{max}}^{\text{OD}} = 0.27, \quad \text{and show the results in the inset of Fig. 1(a). In Fig. 2(b), we also compare the published results for YBCO [14] and the variation of } n_s \text{ from our calculation. The good agreements of calculation and experiments demonstrate that the phase separation can account for the “recurring” behavior of } n_s/m^*(T \to 0) \text{ in the OD region and its anomalously sharp change around } x_c. \]

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FIG. 1. (a) Plot of $T_c$ versus muon spin relaxation rate $\sigma(T \to 0) \propto n_s/m^*$ of HTSC systems in the UD-OPT (open symbols) and OD (closed symbols) regions [1,11,14,20]. Inset shows $T_c$ versus $n_s = x_c p_s$ from the present model for $T_{c_{\text{max}}}$ = 90 and $x_c = 0.19$ [holes/Cu]. (b) Plot of $T_s$ versus the 2-d Fermi temperature $T_F$ ($\propto$ 2-d superfluid density) for $^4$He and $^4$He/$^3$He mixture films adsorbed on Mylar, Vycor and alumina powders [21,22,24]. The solid line represents Kosterlitz-Thouless transition temperature $T_{K_T}$.

FIG. 2. (a) Muon spin relaxation rate $\sigma(T \to 0) \propto n_s/m^*$ (closed circles) [11] and the “gapped” response $\gamma_s$ in the linear-term of the specific heat (open circles) [25] in Tl2201. The broken line illustrates a projected variation of $n_n/m^*$. (b) $\sigma(T \to 0) \propto n_s/m^*$ in YBCO [14] (closed circles) and $n_s(T \to 0) = x_c p_s$ for $x \geq x_c$ and $x$ for $x < x_c$ (open circles) from our model plotted versus hole concentration $x$ [Cu].

FIG. 3. Proposed phase diagram of HTSC systems. For model calculation, the $T_c$ curve is approximated by a parabola and the $T^*$ by a line. The inset illustrates proposed microscopic phase separation in the OD region.
FIG. 4. (a) Temperature dependence of the muon spin relaxation rate $\sigma$ observed in overdoped Tl2201 [11]. (b) Model calculation of $n_s(T) \equiv x_s(T) p_s(T)(1 - (T/T_c)^\beta)$ with $\beta = 3.1$ for $T_c^{\text{max}} = 80$ K and $x_c = 0.19$. (c) Experimental results of $\sigma(T)$ in LSCO [27], compared with the model calculation for $T_c^{\text{max}} = 36.3$ K, $x_c = 0.193$, and $n_s$ given as in (b). $\beta = 2.37$ was obtained by fitting the observed results for Sr 0.15, while the curve for Sr 0.2 represents our model for $x = 0.195$. 