Normal state thermodynamics of cuprate superconductors

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We propose a microscopic explanation of the pseudogap features discovered in the normal state specific heat and magnetic susceptibility of cuprates. In the framework of the bipolaron theory of high-\(T_c\) superconductors we explain the magnitude of the carrier specific heat and susceptibility as well as their universal scaling with temperature over a wide range of doping.

There is strong evidence for the normal state pseudogap in high-\(T_c\) cuprates from magnetic susceptibility [1], specific heat [2], angle-resolved photoemission (ARPES) [3], tunnelling [4], and some kinetic measurements [5]. One view supported by ARPES is that the gap reflects precursor superconducting correlations in the BCS-like state below some characteristic temperature \(T^*\) without long range phase coherence [6]. Testing of this hypothesis with specific heat [2] and tunnelling [4] data, it is found that this view cannot be sustained. In particular, there is no sign that the gap closes at a given temperature \(T^*\), which rules out any role of superconducting phase or spin fluctuations [4]. On the other hand, the strong-coupling extension of the BCS theory based on the multi-polaron perturbation technique firmly predicts the transition to a charged Bose liquid in the crossover region of the BCS coupling constant \(\lambda \simeq 1\) [7]. The (bi)polaronic theory of carriers in cuprates, confirmed by infrared spectroscopy [8] and by the isotope effect on the carrier mass [9], provides a natural microscopic explanation of the normal state gap [10].

At finite temperatures, a fraction of the carriers exist as unpaired hole polarons. These particles are responsible for the magnetic response of the system.

We also employ the simplification that the tunnelling probability between localisation wells is negligible. This allows the partition function \(Z_l\) for the localised part of the system to be written as

\[
Z_l = \prod_i Z_i = 1 + 2e^{(\mu - E_i)\beta} + e^{2(\mu - E_i + \Delta/2)\beta},
\]

where we have assumed the no double occupancy condition. \(\Delta\), \(\mu\) and \(E_i\) are respectively the bipolaron binding energy, chemical potential and a single-particle energy level of the well, whilst \(\beta = 1/k_BT\). The point to note about equation (1) is that the localised partition function cannot be factorised into a product of two particle and one particle partition functions. The physics of localised bipolarons and polarons is thus not separable implying that only one density of states (DOS) profile should be taken for localised particles. The density of localised particles is determined by

\[
n_l = -\frac{\partial \Omega_l}{\partial \mu}
\]
with Ωt = −β−1 log Zl. This gives

\[ n_t = 2 \int_{-\infty}^{0} \rho_l(E)f_l(E)dE \]  

(3)

where

\[ f_l(E) = \{1 + [g(E - \mu - \Delta/2)]^{-1} \}

(4)

with \( g(\xi) = \exp(\xi)cosh(\xi/2 + \beta\Delta/4)\cosh(\xi/2 - \beta\Delta/4) \). \( \rho_l(E) \) refers to the density of localised states per spin. We can then write for the number conservation condition:

\[ 2n_b + 2n_p + n_t = x, \]

(5)

where \( n_{b,p} \) is the density of delocalised bipolarons and polarons, respectively and \( x \) the doping per unit cell. For \( La_{2-x}Sr_xCuO_4 \) \( x \) is given by the atomic concentration of \( Sr \) whilst in \( YBa_2Cu_3O_{7-\delta} \), \( x = 2(1-\delta)/3 \). The free particle density is given by

\[ n_b = \int_0^\infty dE\rho_b(E)f_b(E) \]

\[ n_p = \int_0^\infty dE\rho_p(E)f_p(E) \]

(6)

where \( f_b(E) = \{exp[\beta(E - 2\mu - \Delta)] - 1\}^{-1} \) and \( f_p(E) = \{exp[\beta(E - \mu)] + 1\}^{-1} \), so that equation (5) allows us to determine the chemical potential \( \mu(T) \) if bipolaronic and polaronic DOS, \( \rho_{b,p}(E) \) are known. The finite bipolaron bandwidth, the one-dimensional singularity of (bi)polaronic DOS [14], and a finite width of the localised tail give rise to a Shottky-like anomaly of the specific heat and a Curie-like temperature dependence of the susceptibility which are observed at high temperatures in overdoped samples as explained in Ref. [12]. Here we consider the underdoped region, where the potential wells are deep and impurity-scattering broadening of the Van-Hove singularities (VHS) large due to ineffective screening by carriers. The previous analysis [10,13] showed that the characteristic width of the localised tails and VHS is above room temperature in underdoped samples. We can thus neglect any DOS structure for the relevant temperature range by taking \( \rho_b(E) = \rho_p(E) = 2\rho_l(E) \approx N(0) \) with \( N(0) \) a single-particle DOS at the mobility edge, \( E = 0 \). The bipolaron chemical potential \( 2\mu + \Delta \) is then pinned at the mobility edge, giving \( \mu = -\Delta/2 \), as follows from Eq. [14] for \( k_BT N(0) \ll 1 \). This assumption greatly simplifies further calculations. Including the contribution of delocalised bipolarons, thermally excited polarons and localised carriers we obtain the total energy as

\[ E(T) = E_0 + \frac{N(0)}{\beta^2} \int_0^{\infty} d\xi \{\xi[coth(\xi) - 1] + (4\xi + \beta\Delta)[1 - \tanh(\xi + \beta\Delta/4)] + 2\xi[g(-\xi)^{-1} + 1]^{-1} \}. \]

(7)

Here \( E_0 \) is a temperature independent (negative) constant. As a result we find a universal temperature scaling of the energy, \( E(T) = f(\beta\Delta) \), which allows us to extract the normal state gap from the experimental specific heat \( C = \partial E/\partial T \) without any fitting parameters as shown in Fig.1. In the low-temperature limit, \( \beta\Delta \gg 1 \) we get

\[ g(\xi) \approx \exp(2\xi) \]

and a linear specific heat with an exponential correction

\[ C \approx k_B N(0)\beta^{-1}\left[\frac{\pi^2}{4} + \frac{\beta^2\Delta^2}{2}\exp(-\beta\Delta/2)\right]. \]

(8)

This result is in contrast with an expectation that the specific heat of nondegenerate bipolarons is temperature independent above \( T_c \). The random potential as well as a low-dimensional DOS pins the chemical potential at the mobility edge even in the normal state, so the bipolaron density (and hence the specific heat) is proportional to temperature. The latter leads to a temperature dependent Hall effect [17] and explains other anomalous kinetic properties of cuprates [14]. Half of the bipolaron binding energy \( \Delta/2 \), which is an energy gap between the bottoms of bipolaronic and polaronic bands has been estimated from 400K to 50K depending on doping [14]. In this temperature range one has to calculate \( E(T) \) and \( \gamma = C/T \) by numerical integration of Eq.(7) with the result shown in Fig.1. There is a clear scaling of experimental \( \gamma \) with \( \beta\Delta \) in a wide doping range of \( YBa_2Cu_3O_{7-\delta} \). The corresponding values of \( \Delta \) are shown in Fig.2. They follow the same doping dependence as that determined phenomenologically [14] and are of the same order of magnitude. It should be noted though that the d-wave approach taken by Loram et al gives consistently higher gap values than those found here. Nonetheless, d or s-wave like gaps in the DOS can be
obtained easily within this model by adjusting the nature of the particle-particle interaction or the $k$–dependence of the polaronic energy. Such discrepancies are not thus a significant problem. A drop of $\gamma$ at higher temperatures (Fig.1) is due to a finite bipolaron bandwidth as discussed above.

Following Loram's analysis [17], we compare $\gamma$ with the differential magnetic susceptibility $\chi^* = \partial(\chi(T))/\partial T$. The experimental data for $\chi^*(T)$ are perfectly consistent with our model. There are two contributions to the magnetic response, from delocalised (thermally excited) polarons, $\chi_p$, and from localised ones, $\chi_l$. For the first contribution we obtain by the use of the Kubo formula for free fermion magnetisation,

$$\chi_p(T) = 2\mu_B^2 N(0)[e^{(E/\Delta)2} + 1]^{-1},$$

where $\mu_B$ is the Bohr magneton. The single-well partition function in an external magnetic field, $H$ is given by

$$Z_i = 1 + e^{2(\mu/E - \Delta/2)\beta} + e^{(\mu - E + \mu_B H)\beta} + e^{(\mu - E - \mu_B H)\beta}$$

Differentiating twice the corresponding $\Omega$ potential with respect to the magnetic field yields

$$\chi_l(T) = \mu_B^2 \beta \int_{-\infty}^{0} dE \rho_l(E) f_p (E),$$

where $f_p(E) = [1 + e^{(E/\Delta)/2}e^{(E - \mu - \Delta/2)\beta}]^{-1}$ is the distribution function of localised polarons. If DOS is a constant $\rho_l(E) = N(0)$, and temperature is low, $\beta\Delta \gg 1$ we obtain an exponential temperature dependence of the spin susceptibility as

$$\chi(T) = \chi_p(T) + \chi_l(T) \approx 2\mu_B^2 N(0)(1 + \pi/4)e^{(E/\Delta)/2}.$$

The numerical integration of Eq. (11) for the entire temperature range with the constant DOS yields a universal scaling of $\chi^*$ as a function of $\beta\Delta$. This is nicely confirmed by experiment, as shown in Fig.3. It is remarkable, that with about the same $\Delta$ and DOS (see Fig.2) one can describe both the specific heat and spin susceptibility of underdoped Y Ba$_2$Cu$_3$O$_{7-\delta}$. This is at variance with some opinions that the experimental Wilson ratio is difficult to understand within the framework of our model. In fact, thermally excited polarons provide the spin susceptibility and a finite Wilson ratio close to the experimental one, while the binding energy of bipolarons is responsible for the normal state gap. We may therefore conclude that the formation of real space pairs (bipolarons) above $T_c$ and their partial localisation by the random potential are essential features in describing the normal state thermodynamics of Y Ba$_2$Cu$_3$O$_{7-\delta}$ and other cuprates exhibiting similar normal state gap. The bipolaron theory can explain such non-Fermi liquid features as a large carrier entropy, the gap above $T_c$, temperature dependence of $\gamma$ and $\chi$ and their ratio. Another strong indication of the existence of bipolarons comes from the resistive and thermodynamic measurements in the critical region. A divergent upper critical field was measured in many cuprates as predicted by one of us [18], and the magnetic field dependence of the specific heat jump is just that of the charged Bose-gas [19]. We greatly appreciate the enlightening discussions with A. Blackstead, J.R. Cooper, J.T. Devreese, J.D. Dow, A. Junod, H. Kamimura, W.Y. Liang, J. Loram, J.L. Tallon and G. Zhao.

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Figure Captions

Fig.1 Universal scaling of $\gamma/k_B^2 N(0)$ with $2k_B T/\Delta$ compared with theory (line) for $YBa_2Cu_3O_{7-\delta}$ ($N(0)= 1.17 eV^{-1}$ per spin). Fig.2 Theoretical normal state gap as a function of doping. Fig.3 Universal scaling of the differential spin susceptibility, $\chi^s(T)/\mu_B^2 N(0) = (\chi_{exp}^s - 0.39 \times 10^{-4} emu/mole)/\mu_B^2 N(0)$ compared with theory (line).

For experimental data, see Loram et al [17]
Figure 1: Universal scaling of $\gamma/k_B^2 N(0)$ with $2k_BT/\Delta$ compared with theory (line) for $YBa_2Cu_3O_{7-\delta}$ ($N(0) = 1.17 eV^{-1}$ per spin).
Figure 2: Theoretical normal state gap as a function of doping.
Figure 3: Universal scaling of the differential spin susceptibility, $\chi^*(T)/\mu_B^2 N(0) = (\chi_{exp}^* - 0.39 \times 10^{-4} \text{emu/mole})/\mu_B^2 N(0)$ compared with theory (line).