Condensation energy and the mechanism of superconductivity

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Condensation energy in a superconductor cannot be precisely defined if mean-field theory fails to hold. This implies that in the case of high-temperature superconductors, discussions of quantitative measures of condensation energy must be scrutinized carefully because the normal state is anomalous and the applicability of a mean-field description can be questioned. A related issue discussed here is the precise meaning of a superconducting transition driven by kinetic as opposed to that driven by potential energy; we argue that this is a semantic question.

I. INTRODUCTION

In an earlier paper, Chakravarty, Kee, and Abrahams (CKA),[1] we raised the issue that the notion of superconducting condensation energy[2] is ill defined if the transition cannot be described by BCS mean-field theory, where the system turns into a normal Fermi liquid with no pairing correlations once the superconducting order parameter vanishes. Another purpose of that paper was to elucidate the interlayer tunneling theory (ILT).[3] In particular, we examined the strong version of ILT proposed by Anderson,[4,5] in which the entire "condensation energy" was ascribed to ILT. This proposal turned out to be at variance with the c-axis penetration depth measurements of Moler *et al.*[6] in Tl2201 and was thus falsified. Nevertheless, we were interested in understanding if it is at all possible that ILT plays an important role in enhancing the transition temperature T_c by increasing the bare superfluid density, thus defining ILT in a weaker sense, as an enhancement mechanism over and above an in-plane pairing mechanism.[7]

CKA also noted that nominally optimally doped Tl2201 has a specific heat peak[8] that could be approximately fitted by a two-dimensional (2D) Gaussian fluctuation contribution to the free energy. This observation reflects once again the importance of in-plane pairing correlations and was an important conclusion of CKA. We then asked if there was a sensible procedure to subtract the 2D fluctuations and use the remainder of the free energy to understand the effect of ILT in the weaker sense of enhancement of the bare superfluid stiffness. This was difficult, as the correctness and the precision of the specific heat measurements[8] were unknown and still are because the measurements are yet to be reproduced by a second group. In addition, it was not clear over what range of temperatures the fluctuation contributions must be fitted. Of course, the very notion of Gaussian fluctuations in a 2D superconducting transition cannot be meaningful close to the transition. Despite these difficulties, an approximate subtraction procedure was used by CKA. The result was that the enhancement of the bare superfluid stiffness in Tl2201 was indeed extremely small. Nonetheless, we believe that it is conceptually important to perform such subtractions, preferably more accurate ones, to estimate the effects of ILT.

This is also true for multilayer cuprates, where superficially ILT seems to be important,[9] at least in the weaker sense defined earlier.

To this day, the cause of a striking systematic rise and a subsequent drop in T_c for a homologous series as a function of the number of layers in the unit cell is not known. Even if we ascribe the rise to the enhancement due to ILT,[10] the drop must be ascribed to a competing mechanism that develops with the increase in the number of layers, perhaps because the inner layers have a tendency to become underdoped. A homologous series of cuprate superconductors is a family in which each member has the same charge-reservoir block, but n CuO$_2$ planes in the infinite-layer block, which consists of $(n-1)$ bare cation planes and n CuO$_2$ planes.[11] Clear systematics of T_c is only evident within a given homologous series. A well-studied example[12] is the family HgBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+\delta}$ whose T_c, optimized with respect to oxygen concentration, as a function of n, is shown in Fig. 1. The formal copper valence $v_{\mathrm{Cu}} = 2(n+\delta)/n$ is also a bell-shaped curve that peaks at $n=3$. Similar results are known for other families, for which the transition temperatures follow a similar pattern, often peaking at $n=3$ or 4. The issues
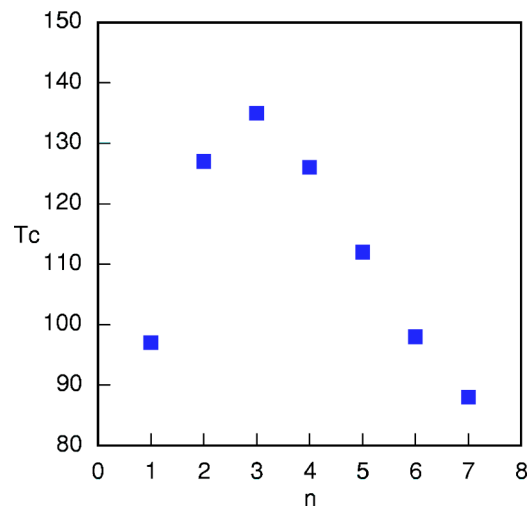

FIG. 1. Transition temperature across a homologous series: HgBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+\delta}$, adapted from Ref. 12.

of the dependence of T_c on the number of layers and the role of ILT remain unresolved.

We now address the basic question raised by CKA, namely, is condensation energy a precise quantitative concept for high-temperature superconductors? Given the interest that this subject still elicits,[9,13–18] we have decided to publish this brief note to elaborate further on condensation energy and on a related theoretical question: can the mechanism of superconductivity be usefully said to be driven by kinetic as opposed to potential energy? We argue, in answer to the first question, that there are *no* general arguments, thermodynamic or microscopic, that can lead to a precise and quantitative definition of the condensation energy. It is truly an approximate concept and may not be suitable for high-temperature superconductors for a variety of reasons. The answer to the second question is that while it is important to identify the mechanism by which the condensate is formed, it is a semantic issue as to whether or not we describe the transition as driven by potential or kinetic energy.

II. CONDENSATION ENERGY

Colloquially, the condensation energy is the difference of the ground-state energies between the normal state and the superconducting state. A little thought reveals several related problems.

(1) What do we mean by the normal state? In particular, what if there are other broken symmetries[19–23] in the regime in which there is no superconductivity and a further transition to the unbroken symmetry state at a temperature above the superconducting T_c?

(2) What if the normal state contains superconducting fluctuations?

(3) What if the normal state changes as a function of the magnetic field, or other tuning parameters used to destroy the superconducting state?

(4) What if the transition to the normal state is not a first-order transition, such that one cannot meaningfully define a notion of a metastable state that can be accessed in the experiments?

(5) How should one correctly extrapolate the nonzero temperature measurements to $T=0$ to access the hypothetical normal state with the same set of parameters for which nature actually provides us with the superconducting state?

There are indeed simplifying situations, where the complexities mentioned above do not arise in the practical sense.[2] Thus, when mean-field theory holds and the normal state is a Fermi liquid with no measurable trace of pairing correlations, the simplest extrapolation of the normal state below T_c with the specific heat $C(T)=\gamma T$, where γ is a constant, is plausible, assuming that there are no other instabilities of the Fermi liquid at temperatures below T_c. One may further constrain this extrapolation by entropy conservation because the difference of entropies between the normal state and the superconducting state is zero at the mean-field T_c and at $T=0$ (Ref. 2).

For high-temperature superconductors, there are great many complexities. The presence of a pseudogap, quite unlike a BCS superconductor, makes the extrapolation of the normal state (in fact, even its definition) exceedingly problematic. If the magnetic field H is used as a tuning parameter to destroy superconductivity, its large magnitude, $H>H_{c2}$, may stabilize some other ordered state.[24] Moreover, unlike conventional superconductors, for which the effect of the magnetic field in the normal metal is a weak Landau diamagnetism, the normal state of high-temperature superconductors may not be so impervious to such high fields necessary to destroy superconductivity. The attempt to destroy superconductivity by doping Zn to replace Cu suffers from similar problems. In fact, it is empirically known that Zn impurities introduce magnetic order in high-temperature superconductors.[25]

There are even more fundamental reasons for doubting the notion of condensation energy. If the transition is a continuous transition, there is no way that one phase can be continued into the other beyond the transition. Therefore, the hypothetical normal state cannot exist for the same set of parameters for which the superconducting state is more stable; the notion of a metastable state is thus not meaningful for a continuous transition. An exactly solved model illustrates this point beautifully. Consider the 2D Ising model for which Onsager's result for the free energy is known for all temperatures. The analytic continuation of the free energy f_+ from above the ferromagnetic transition point T_F to below T_F was obtained exactly by Majumdar.[26] One gets, close to T_F,

$$f_+ \simeq - \frac{k_B T_c}{4\pi u_F^2}(u-u_F)^2[\ln|u-u_F|+i\pi], \tag{1}$$

where $u=\exp(-4J/k_B T)$, u_F is its value at the transition point T_F, and $J>0$ is the ferromagnetic exchange constant. It is seen that the analytic continuation acquires an imaginary part, which has no obvious physical meaning. This is true for any continuous transition for which specific heat exhibits a nonanalytic critical singularity, reflecting a branch point in the complex plane. It is even true for infinite order transitions, as in a six-vertex model. The exact analytic continuation of the free energy of the six-vertex model was obtained by Glasser, Abrahams, and Lieb[27] If the transition were instead a first-order transition, the imaginary part of the free energy could be interpreted as the decay of the metastable state.[28]

It might be tempting to define condensation energy as the difference between the exact ground-state energy with zero-order parameter (unbroken symmetry state) and the exact ground-state energy with a prescribed finite value of the order parameter (broken symmetry state). For a broken symmetry with a nonconserved order parameter, as in a superconductor, this is impossible, simply because the order parameter and the hamiltonian cannot be simultaneously diagonalized. To understand the nature of the broken symmetry state with a nonconserved order parameter, consider the simplest such case: an antiferromagnet for which the staggered order parameter is not conserved. In a bipartite lattice, where the Marshall sign condition[29] holds, the ground state is always a singlet. In a finite volume, the symmetry cannot be broken, and, for a large system, the order parameter will precess slowly so that no orientation is preferred. The effec-

tive Hamiltonian $\mathcal{H}_{\text{eff}}$ that describes this precession depends on the total spin $\mathbf{S}_{\text{tot}}$ and is that of a rotor, given by

$$\mathcal{H}_{\text{eff}} = \frac{1}{2\chi} \mathbf{S}_{\text{tot}}^2 = \frac{1}{2\chi} S(S+1), \qquad (2)$$

where $\chi = N \chi_s^{\perp}$ is the total spin susceptibility, in units of $g\mu_B$, $\hbar = 1$; $\chi_s^{\perp}$ is the susceptibility per spin with respect to a local uniform magnetic-field-oriented perpendicular to the staggered order parameter. One can imagine deriving this Hamiltonian by a renormalization group analysis, as the relevant states are all below the one-magnon state of the smallest nonzero momentum in a box. Even though the actual eigenstates are those of total spin, as $N \rightarrow \infty$, a tower of excited states collapses to the singlet ground state corresponding to $S=0$, and becomes degenerate with it in the thermodynamic limit.[30] The broken symmetry state with a fixed direction of the staggered order parameter is a coherent superposition in this quasidegenerate manifold. Thus, the energetic difference with the singlet ground state vanishes in the limit $N \rightarrow \infty$. The energetic difference between the normal state and the condensed state is identically zero.

Intuitively, one feels that one should be able to define condensation energy variationally. Consider two variational wave functions, one of which corresponds to the superconducting state with broken $U(1)$ gauge symmetry, and the other corresponding to the normal state. Of course, we have to define what we mean by the normal state—a Fermi liquid, a state with another broken symmetry, etc. Similarly, we must also define the order parameter symmetry in the superconducting state. Given a Hamiltonian, we can now calculate the expectation value with respect to these states and find the difference in energy, and hence condensation energy. This is not only model dependent but also calculation dependent. More importantly, there is no known experimental method to check the correctness of this definition of the condensation energy.

There is one instance in which the condensation energy can be defined with little ambiguity,[2] and that is for a type I superconductor. In this case, the transition to the normal state as a function of a magnetic field is a first-order phase transition with only a finite correlation length. If the normal state is relatively insensitive to the applied magnetic field necessary to destroy superconductivity, the measurement of the thermodynamic critical field H_c, as $T \rightarrow 0$, immediately gives the condensation energy from the formula

$$G_n - G_s = \Omega \frac{H_c^2}{8\pi}, \qquad (3)$$

where G is the Gibbs free energy, and Ω is the volume of the sample. Unfortunately, this is unusable for high T_c superconductors because they are of type II.

III. FRUSTRATED KINETIC ENERGY

An idea that has been discussed often is that the superconductivity in the cuprates is driven by the saving of the electronic kinetic energy in the superconducting

state.[1,3,7,31–33] There are some experiments[9,34,35] that could be interpreted in this manner.

Cuprates are complex materials with intricate electronic structure. If we assume that electron-phonon interactions do not play a major role, the problem is entirely electronic in nature. For concreteness, let us assume that a single band two-dimensional Hubbard model is a good effective Hamiltonian to understand the low-energy properties, including the superconductivity of these materials. Even if the electronic Hamiltonian were more complicated, it would make no difference to our basic argument. For example, we could also incorporate electron-phonon interaction at the expense of making the discussion more complex. The one-band Hubbard model describes processes smaller than energy U and is

$$H_{\text{eff}} = -t \sum_{\langle ij \rangle} (c_{i\sigma}^{\dagger} c_{j\sigma} + \text{H.c.}) + U \sum_{i} n_{i\uparrow} n_{i\downarrow}. \qquad (4)$$

The higher energy processes are assumed to be adiabatically decoupled from the lower energy processes. Here $c_{i\sigma}$ is an electron destruction operator of spin σ, and $n_{i\sigma}$ is the corresponding density operator.

When U is large, the model can be reduced to the effective Hamiltonian called the t-J model, which is

$$H_{t-J} = -t \sum_{\langle ij \rangle} (c_{i\sigma}^{\dagger} c_{j\sigma} + \text{H.c.}) + J \sum_{\langle ij \rangle} (\mathbf{S}_i \cdot \mathbf{S}_j - \tfrac{1}{4} n_i n_j), \qquad (5)$$

with $J = 4t^2/U$, together with the constraint $n_i \leq 1$. The operators $c_{i\sigma}$ still satisfy the fermion anticommutation rule, but one must constrain the Hilbert space. This can be done by examining the eigenvalue of a local operator n_i.

The J term is a reflection of the frustrated kinetic energy at the level of the Hubbard model[36] in the $U \rightarrow \infty$ limit, but at the level of the t-J model, the J term cannot be properly defined to be kinetic energy: it does not represent motion of the particles described by the fermion operators. Moreover, it is neutral under gauge transformation, because both $\mathbf{S}_i$ and n_i are neutral. In contrast, the t term is the kinetic energy; it picks up a Peierls phase under a gauge transformation and the constraint, being local, remains unchanged. Thus, it *is* meaningful to ask which term plays a more important role if the superconductivity is described by the t-J model, but it is pure semantics to try to pin the mechanism down as being driven by kinetic as opposed to potential energy. What is potential energy at one level is kinetic at the other. If the t-J model is not adequate to describe superconductivity, we must return to the Hubbard model, and the partitioning of the kinetic and potential energies will be different.

It is useful to examine the BCS theory of superconductivity for which the effective Hamiltonian is the reduced Hamiltonian. A textbook calculation shows that the kinetic energy is increased in the superconducting state, $\delta(KE) = (\Delta^2/V) \times [1 - N(0)V/2]$, while the potential energy is lowered, $\delta(PE) = -\Delta^2/V$, due to the attraction of electrons mediated by phonons. Here Δ is the superconducting gap, V is the magnitude of the attractive interaction, and $N(0)$ is the density of states at the Fermi energy. Although the phonon exchange is a kinetic process, its effect is correctly described as

a potential energy at the level of the reduced Hamiltonian. The increase of the kinetic energy is not in the least surprising because BCS superconductivity develops on top of a Fermi liquid in which the kinetic energy is diagonal and unfrustrated. Therefore, it must necessarily be increased in the superconducting state. An interesting corollary is that if superconductivity is due to the lowering of the electronic kinetic energy in a suitable low-energy effective Hamiltonian, it could not develop on top of a Fermi liquid state, for in a Fermi liquid the kinetic energy operator is diagonal; the normal state will have to be a non-Fermi liquid. We may have a new class of superconductors, but it is still semantics to say that it is driven by kinetic energy, for it will surely depend on the low-energy effective Hamiltonian, in which a part can appear as a potential energy, which could be a reflection of frustrated kinetic energy at the preceding level.

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[10] There is a common misconception that a suiatble Lawrence-Doniach model can reproduce the systematics of T_c. This is simply incorrect and is discussed in detail in Ref. 7. An enhancement is possible if the coupling between the layers is mistakenly taken to be $-(\psi_n^*\psi_{n+1}+\text{c.c.})$ instead of $|\psi_n-\psi_{n+1}|^2$, where ψ_n is the order parameter for the nth layer. For a conventional superconductor, the Josephson energy is proportional to $[1-\cos(\phi_n-\phi_{n+1})]$, not $-\cos(\phi_n-\phi_{n+1})$. Moreover, in a BCS superconductor, the density of states is changed very little by the small hopping matrix elements of the electrons between the layers. Consequently, there is little effect on T_c^0 from the density of states. The interlayer coupling can, of course, suppress phase fluctuations, thereby raising the true T_c closer to T_c^0. This mechanism was indeed explored, but it led only to small enhancements of T_c [E.W. Carlson *et al.*, Phys. Rev. Lett. **83**, 612 (1999)], far from the data shown in Fig. 1.

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