Structure of the Electrical Double Layer in High-Temperature Superconductors. Origin of the Dip in the Double-Layer Capacitance near the Superconducting Transition

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A theory of the electrical double layer in high-temperature superconductors is developed in the context of a modified Ginzburg−Landau equation. Potential and excess charge distributions inside the electrode are computed. These distributions are shown to be characterized by a new fundamental length parameter. This length diverges when the electrode temperature approaches the superconducting critical temperature. The capacitance of the electrical double layer is found to be inversely proportional to this length. On the basis of this analysis, the origin of an experimentally observed dip in the double-layer capacitance is explained. The dependence of this capacitance dip on the external field is predicted.

I. Introduction

Since the remarkable discovery of high-temperature superconducting (HTSC) materials,[1] great interest has grown in the electronic properties of these important systems. In this study we are particularly interested in the electron transfer processes between a superconducting electrode and reactants in liquid or solid solutions that are in contact with the electrode. The electronic properties determine the structure of the electrical double layer near the electrode and the capacitance of this double layer.

Recently, several laboratories,[2−5] have explored the chemical aspects of HTSC interfaces with chemical materials that are in the "normal" conducting state. Lorenz et al.[2] observed changes in the electrochemical reaction impedance of the Ag^+/Ag couple at a solid electrolyte/HTSC electrode interface as the temperature crosses the superconducting transition temperature, T_c. Recently, Murray and co-workers reported the discovery of remarkable electrolytic fluids that enabled solution electrochemical measurements at temperatures as low as 88 K.[4] The availability of such solvents has allowed a revolutionary electrochemical experiment in which the influence of superconductivity on solvent/high-T_c interfaces can be explored for the first time. Using ethyl chloride and butyronitrile (EtCl/BuCN) containing Bu_4NClO_4, a T_c-correlated dip in the electrochemical double-layer capacitance of two different types of HTSC electrodes was observed together with T_c-correlated changes in the electrode reduction kinetics.[5] The T_c-correlated double-layer capacitance effect and the unchanged (in situ) T_c following electrochemical experimentation demonstrated that the superconducting characteristics of the HTSC were not destroyed by contact with the electrolyte solution or by the electrochemistry.

The remarkable electrochemical properties of HTSC materials have not yet been explained theoretically. A critical challenge is to develop a theory describing the T_c-correlated dip in the electrochemical double-layer capacitance and the T_c-correlated changes in the reduction kinetics at the electrode. These phenomena are very important because many electrochemical properties depend on the capacitance of the double layer and on the electron transfer kinetics at the electrode. In addition, exploration of the electrochemical properties of the HTSC materials can provide valuable information about the mechanism of high-temperature superconductivity, which remains poorly understood. There have been a number of prior attempts to explain the electrochemical phenomena of HTSCs. Kuznetsov developed a theory of electron transfer between superconducting electrodes and electrolyte solutions and in other studies examined the jump in the current observed in the vicinity of the superconducting transition.[6] Zusman et al.[7] also examined electron transfer between the superconductors and electrolyte solutions. In these studies the jump in the derivative of the electron transfer rate vs temperature at the superconducting transition temperature was predicted as well as other current−voltage characteristics of HTSC materials. However, the first explanations of the dip in the electrochemical double-layer capacitance appeared only recently.[8] Phillips used the idea that the HTSC structure is inhomogeneous in space. In the present analysis, we propose an alternative explanation of the double-layer phenomena using a different strategy that explains the origin of the dip in the double-layer capacitance without assuming spatial inhomogeneity of the HTSC material. We show that the dip in the double-layer capacitance can be explained in the framework of the usual Ginzburg−Landau theory modified to account for charge penetration into the superconductor.

In superconductors at temperatures below the critical temperature, T_c, electrons are bound in Cooper pairs,[9] with the effective size of these pairs defined by the coherence length ξ_0. Essentially, charge added to the superconductor will be distributed in these pairs. Interesting and important questions concern the spatial distribution of this added charge and the equation that describes this charge distribution. A related question is what the electric field associated with this charge is within the superconductor. To answer these questions, we have derived a modified Ginzburg−Landau equation for the wave function $\psi(\vec{r})$ of the Cooper pair. This equation describes how the wave function changes upon addition of charge. The simplicity of the final expressions arising from this modified Ginzburg−Landau equation allows us to analyze the electrochemical aspects of the above questions. For example, we are able to explain the origin of the dip observed in the electrical double-layer capacitance near T_c. We also predict in this paper that the charge distribution and electric field penetration into the

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superconductor is characterized by a new fundamental length, λ_{ZB}, which differs from other fundamental lengths characterizing superconductivity. This new length describes how rapidly the charge distribution and electric field decay as they penetrate the superconductor. The length is in some sense similar to the Debye length in electrolyte solutions.

For comparison purposes, we review the fundamental distances (coherence length, magnetic field penetration depth) that are essential to describe the superconducting properties of electrodes. The coherence length is the parameter that characterizes the size of the Cooper pairs that are the main charge carriers responsible for superconductivity. The magnetic field penetration depth (or the so-called London length) is the parameter that characterizes the distance at which a magnetic field applied to a superconductor is totally screened by superconducting currents that arise in response to the magnetic field. In this paper, we have attempted to present the results in such a way that the mathematics need not overwhelm the reader. In doing so, it is necessary to discuss some well-known ideas in order to emphasize the new ones. In addition, the calculations require a certain amount of manipulation that is important for completeness. These manipulations appear in the Appendix.

The principal results of this paper are (1) a modified Ginzburg−Landau equation and (2) expressions for the charge distribution and the electrical potential distribution inside the superconductor. The key new result is a simple formula for the capacitance of the electrical double layer in the vicinity of the superconducting transition. This new formula explains the origin of the dip in capacitance observed experimentally[5] as the superconducting transition is approached.

This paper is organized as follows. In section II, we discuss the approximations used to describe the distribution of added charge in terms of the modified Ginzburg−Landau equation, and we derive this equation. Section III details the computation of the charge density distribution and the electrical potential inside the electrode. The temperature dependence of the electrode capacitance is discussed in section IV. We conclude in section V.

II. Modified Ginzburg−Landau Equation

Consider an electrode in the superconducting state. If the electrode temperature is not too close to T_c (the consequences of this assumption will be discussed later), most of the electrons are condensed in Cooper pairs. The density of Cooper pairs in the superconductor in the absence of an electric field is proportional to ψ_0^2, where ψ_0 is the wave function of the pair, or the order parameter.[9] ψ_0 obeys the Ginzburg−Landau equation.[9]

$$-\frac{\hbar^2}{2m^*}\nabla^2\psi_0 + \alpha\psi_0 + \beta\psi_0^3 = 0 \tag{1}$$

where $m^* = 2m$, m is the electron mass, and $\hbar$ is Planck's constant divided by 2π. The Ginzburg−Landau equation (eq 1) provides a phenomenological description of superconductivity. The equation is derived by (1) writing the free energy density of the superconductor as a series expansion in powers of ψ_0^2, (2) adding a term proportional to the gradient of ψ_0 squared (analogous to a quantum mechanical kinetic energy term), (3) integrating this free energy density over space, and (4) finally varying ψ_0 to minimize the free energy. The phenomenological parameters α and β are properties of a given superconductor. We use this relatively simple approach because it captures the characteristic length scales at play near the superconducting transition temperature.

When an external potential is applied to the electrode, excess charge enters the electrode and the density of Cooper pairs changes near the boundary of the superconductor. Although the existing experiments[2−5] involve the contact of an electrode with an electrolyte solution, the theory developed in this paper is sufficiently general to describe any charging of the HTSC (in contact, for example, with a non-ionic dielectric fluid). The density of these pairs is now proportional to $\psi^2(\vec{r})$, where $\psi(\vec{r})$ is the wave function of the pair (or the order parameter) changed by the presence of the excess charge. In the absence of excess charge, the superconductor is electroneutral. Therefore, after adding the excess charge q, the density of excess charge ρ will become proportional to the difference $\psi^2(\vec{r}) - \psi_0^2$, i.e.

$$\rho(\vec{r}) = 2e(\psi^2(\vec{r}) - \psi_0^2) \tag{2}$$

Here, $2e$ is the charge of the Cooper pair (e is the electron charge). By definition,

$$\int \rho(\vec{r})\, d\vec{r} = q \tag{3}$$

The interaction energy between this charge density and the electrical potential $\phi(\vec{r})$ that this charge density creates is

$$V_{int} = \rho(\vec{r})\,\phi(\vec{r}) \tag{4}$$

Now we can write the free energy, F, of the superconductor in this potential. F becomes

$$F = \int d\vec{r}\left\{-\frac{\hbar^2}{2m^*}(\nabla\psi)^2 + \alpha\psi^2 + \beta\psi^4 + 2e\phi(\vec{r})[\psi^2(\vec{r}) - \psi_0^2] + \frac{(\nabla\phi)^2}{8\pi}\right\} \tag{5}$$

The first three terms in the free energy functional are the usual Ginzburg−Landau terms.[9] The fourth term describes the interaction of the excess charge with the potential, and the fifth term describes the energy associated with the electric field.

To find the modified equations for the order parameter, we minimize the free energy with respect to (1) the order parameter $\psi(\vec{r})$ and (2) the electrical potential distribution, while maintaining the constraint of eq 3. Minimizing the free energy functional (of eq 5) subject to the constraint of eq 3 leads to the following modified Ginzburg−Landau equation for the order parameter:

$$-\frac{\hbar^2}{2m^*}\nabla^2\psi + \alpha\psi + 2e\phi(\vec{r})\psi + \beta\psi^3 = 0 \tag{6}$$

where the potential $\phi(\vec{r})$ can be found self-consistently from the Poisson equation

$$\nabla^2\phi = -(4\pi)(2e)[\psi^2(\vec{r}) - \psi_0^2] \tag{7}$$

Minimizing the functional (eq 5) also gives the boundary condition

$$(\nabla)_n\psi = 0 \tag{8}$$

where the subscript n designates the component normal to the surface of the electrode. The nonlinear equations (eqs 6 and 7) can be solved using a conventional linearization procedure where possible or by using variational or numerical methods as required.

III. The Charge Density Distribution and Potential inside the Electrode

The electrical potential and charge density distributions inside an electrode can be found analytically for some simple electrode

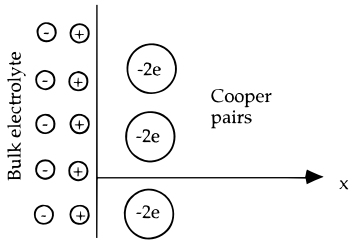

Figure 1. Boundary between the electrode and the bulk electrolyte.

models. We consider here the simplest possible electrode model, namely, a semi-infinite electrode with a planar boundary between the electrode and electrolyte. The electrode model is shown schematically in Figure 1. In this model, the one-dimensional coordinate x is orthogonal to the electrode boundary.

If the charge q is not very large and the temperature of the electrode is not too close to the critical temperature, the order parameter ψ can be written as

$$\psi(x) = \psi_0 + \delta\psi(x) \tag{9}$$

where

$$|\delta\psi(x)| \ll \psi_0 \tag{10}$$

In this case, we can reduce the nonlinear equations (6 and 7) to approximate linear equations for $\delta\psi(x)$. To derive these equations, we substitute ψ from eq 9 into eqs 6 and 7 and expand the nonlinear terms in a series up to terms first order in $\delta\psi(x)$. This linearization procedure gives the following equations for $\delta\psi(x)$:

$$\frac{d^2\phi(x)}{dx^2} = -16\pi e\psi_0\,\delta\psi \tag{11}$$

$$-\frac{\hbar^2}{2m^*}\frac{d^2\delta\psi}{dx^2} + \alpha\delta\psi + 2e\phi(x)\psi_0 + 3\beta{\psi_0}^2\,\delta\psi = 0 \tag{12}$$

with the boundary conditions

$$\left.\frac{d\delta\psi}{dx}\right|_{x=0} = 0 \tag{13}$$

and

$$\left.\frac{d\phi(x)}{dx}\right|_{x=0} = 4\pi q \tag{14}$$

where q is now the surface charge per unit area. Using eq 12, we can eliminate $\delta\psi$ from eq 11 and obtain the simple closed equation for just the potential:

$$\frac{d^4\phi}{dx^4} - \frac{2}{\xi^2(T)}\frac{d^2\phi}{dx^2} + \frac{32\pi e^2}{\beta\xi^2(T)}\phi = 0 \tag{15}$$

with the boundary conditions

$$\left.\frac{d^3\phi}{dx^3}\right|_{x=0} = 0, \quad \left.\frac{d\phi}{dx}\right|_{x=0} = 4\pi q \tag{16}$$

$$\phi(x) \to 0 \quad \text{as} \quad x \to \infty \tag{17}$$

Here $\xi(T)$ is the coherence length[9]

$$\xi^2 = \frac{\hbar^2}{2m^*|\alpha|} \tag{18}$$

In deriving eq 15, we also use the fact that[9]

$${\psi_0}^2 = -\frac{\alpha}{\beta} \tag{19}$$

Equation 15 is solved in the Appendix. The solution is

$$\phi(x) = -\frac{4\pi q\lambda_{ZB}}{\sqrt{2}}\exp\left(-\frac{x}{\lambda_{ZB}}\right)\cos\left(\frac{x}{\lambda_{ZB}} + \frac{\pi}{4}\right) \tag{20}$$

where λ_{ZB} is a new fundamental length parameter that characterizes how rapidly the electric field decays as it penetrates the superconductor. λ_{ZB} is

$$\lambda_{ZB} = \frac{K^{1/2}}{\left(137\dfrac{m^*e^2}{\hbar^2}\right)^{1/2}}\,\xi(T)^{1/2} \tag{21}$$

where K is the so-called Ginzburg−Landau parameter of the superconductor.[9] Using eq 20 for the potential, we find (see the Appendix) the following expression for the charge density:

$$\rho(x) = \frac{q\sqrt{2}}{\lambda_{ZB}}\exp\left(-\frac{x}{\lambda_{ZB}}\right)\sin\left(\frac{x}{\lambda_{ZB}} + \frac{\pi}{4}\right) \tag{22}$$

From eq 22, we see that λ_{ZB} also characterizes the distribution of excess charge inside the superconductor.

The deviation of the order parameter, $\delta\psi(x)$, is also derived in the Appendix. It is

$$\delta\psi(x) = -\frac{q\sqrt{2}}{4e\psi_0\lambda_{ZB}}\exp\left(-\frac{x}{\lambda_{ZB}}\right)\sin\left(\frac{x}{\lambda_{ZB}} + \frac{\pi}{4}\right) \tag{23}$$

The potential and charge distributions appear in Figures 2 and 3. These figures show that the potential and the charge density decay and oscillate as they penetrate the electrode.

The coherence length, $\xi(T)$, diverges as the temperature of the electrode approaches the critical temperature T_c according to the relation[9]

$$\xi(T) = 0.74\xi_0\left(\frac{T_c}{T_c - T}\right)^{1/2} \tag{24}$$

Because the fundamental length λ_{ZB} (see eq 21) is proportional to $\xi^{1/2}$, it also diverges according to the relation

$$\lambda_{ZB} = \frac{0.86K^{1/2}\,\xi_0^{1/2}}{\left(137\,\dfrac{m^*e^2}{\hbar^2}\right)^{1/2}}\left(\frac{T_c}{T_c - T}\right)^{1/4} \tag{25}$$

The order parameter ψ_0 approaches zero as T approaches T_c according to the relation

$$\psi_0 = 26.1\left(\frac{m^*e^2}{\hbar^2}\right)^{1/2}\frac{1}{K\xi_0}\left(\frac{T_c - T}{T_c}\right)^{1/2} \tag{26}$$

(This can be shown by combining eqs 18, 19, and A7). Therefore, substituting eqs 25 and 26 into eq 23, we see that $\delta\psi(x)$ also diverges near T_c. Hence, the criterion of validity (eq 10) for the linearization procedure fails for temperatures sufficiently close to T_c. It follows from eq 23 that the linearization procedure is applicable when

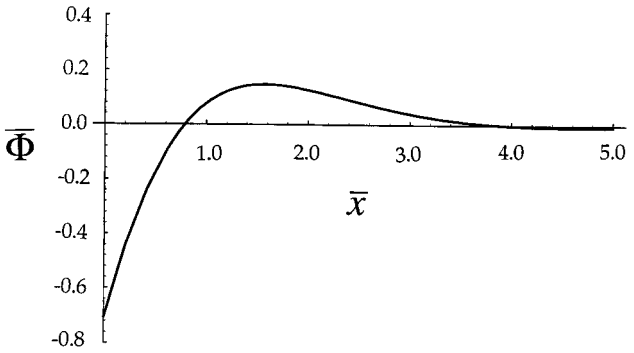

Figure 2. Dependence of the potential on $\bar{x} = x/\lambda_{ZB}$. $\bar{\phi}$ is the dimensionless potential, equal to $\phi\sqrt{2}/4\pi q\lambda_{ZB}$. (The potential here is the negative of the electrode potential of zero charge.)

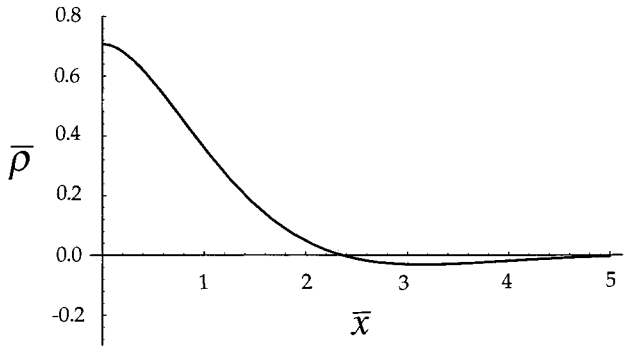

Figure 3. Dependence of the charge density on $\bar{x} = x/\lambda_{ZB}$. $\bar{\rho}$ is the dimensionless charge density, equal to $\rho\lambda_{ZB}/\sqrt{2}\,q$.

$$\frac{q}{4e\psi_0{}^2\lambda_{ZB}} \ll 1 \tag{27}$$

Substituting eqs 25 and 26 into eq 27, we obtain the criterion

$$\frac{T_c - T}{T_c} \gg 0.0044\left(\frac{\hbar^2}{m^*e^2}\right)^{2/3}\xi_0{}^2K^2\left(\frac{q}{4e}\right)^{4/3} \tag{28}$$

Because $q = E_{ext}/4\pi$, where E_{ext} is the external electric field, we finally obtain

$$\frac{T_c - T}{T_c} \gg 2.37 \times 10^{-5}\left(\frac{\hbar^2}{m^*e^2}\right)^{2/3}\xi_0{}^2K^2\left(\frac{E_{ext}}{e}\right)^{4/3} \tag{29}$$

If the electrode temperature is closer to T_c than the criterion (eq 29) allows, eqs 20, 22, and 23 are no longer valid, and we must solve the nonlinear equations (6 and 7) using variational or numerical methods.

IV. Capacitance

Using eq 20 for the electrical potential distribution inside the superconductor, we can find the capacitance of the electrode. Indeed, the capacitance of the electrode, C_e, and the potential of the electrode, $\phi(0)$, are related by the usual expression

$$C_e = \frac{q}{|\phi(0)|} \tag{30}$$

Substituting $\phi(0)$ from eq 20 into eq 30, we obtain the simple result

$$C_e = \frac{1}{2\pi\lambda_{ZB}} \tag{31}$$

As mentioned above, the fundamental length λ_{ZB} diverges as the temperature approaches T_c. Hence, we see from eq 31 that the capacitance of the electrode has a deep dip near the critical temperature. Substituting eq 25 into eq 31, we find the temperature dependence of the electrode capacitance,

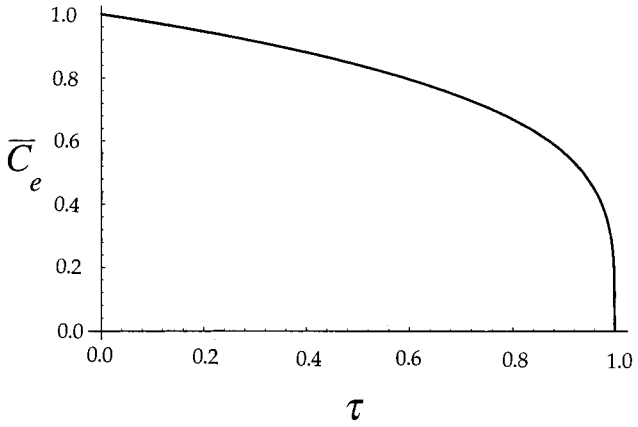

Figure 4. Temperature dependence of the electrode capacitance. τ is the dimensionless temperature equal to T/T_c. $\bar{C}_e$ is the dimensionless capacitance, equal to $[C_eK^{1/2}\xi_0{}^{1/2}(\hbar^2/m^*e^2)^{1/2}]/2.167$.

$$C_e = 2.166K^{-1/2}\xi_0{}^{-1/2}\left(\frac{\hbar^2}{m^*e^2}\right)^{-1/2}\left(\frac{T_c - T}{T_c}\right)^{1/4} \tag{32}$$

This temperature dependence is shown in Figure 4. In reality, of course, C_e does not drop to zero because eq 32 is not valid when

$$\frac{T_c - T}{T_c} < (2.37 \times 10^{-5})\left(\frac{\hbar^2}{m^*e^2}\right)^{2/3}\xi_0{}^2K^2\left(\frac{E_{ext}}{e}\right)^{4/3} \tag{33}$$

At these temperatures, eq 32 is no longer applicable. Substituting eq 33 into eq 32, we estimate the minimum capacitance of the electrode, C_e^{min}, to be

$$C_e^{min} = 0.15\left(\frac{m^*e^2}{\hbar^2}\right)^{1/3}\left(\frac{E_{ext}}{e}\right)^{1/3} \tag{34}$$

From eq 34, we see that the minimum capacitance of the electrode is moderately dependent on the external electric field. As the external field increases, the dip in the capacitance becomes increasingly shallow. This is exactly the behavior observed in the experiments.[5] The temperature dependence predicted by eq 32 and the field dependence of C_e^{min} (eq 34) explain the observed T_c-correlated dip in the double-layer capacitance.[2,5]

V. Conclusions

We have used a modified phenomenological theory of superconductivity to describe the electrical potential and the distribution of excess charge inside a superconducting electrode. The computed potential distribution allowed us to find the temperature dependence of the electrode capacitance near the superconducting transition temperature. This predicted capacitance was shown indeed to contain a sharp dip near the superconducting transition temperature. This conclusion is in agreement with observations.[2,5] This theory also predicts that the dip should become shallower with increasing applied electric field, in qualitative agreement with the experimental data.[5] It would be of great interest to test quantitatively the predicted dependence of the dip magnitude on the applied electric field (eq 34).

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Appendix

In this Appendix we solve eq 15. The general solution of eq 15 is[10]

$$\phi(x) = C_1 e^{k_1 x} + C_2 e^{k_2 x} + C_3 e^{k_3 x} + C_4 e^{k_4 x} \qquad \text{(A1)}$$

where k_1, k_2, k_3, and k_4 are eigenvalues of eq 15 and C_1, C_2, C_3, and C_4 are arbitrary coefficients. Eigenvalues can be found from the roots of the corresponding secular equation

$$k^4 - \frac{2}{\xi^2} k^2 + \frac{32\pi e^2}{\beta \xi^2} = 0 \qquad \text{(A2)}$$

This equation can be solved readily and its solution is

$$k_{1,2,3,4} = \mp \frac{1}{\xi}\left[1 \pm \left(1 - \frac{32\pi e^2 \xi^2}{\beta}\right)^{1/2}\right]^{1/2} \qquad \text{(A3)}$$

Using eq A3, we see that the third and fourth terms in eq A1 tend toward infinity as $x \rightarrow \infty$. From the boundary condition (eq 17), $\phi(x) \rightarrow 0$ as $x \rightarrow \infty$, and we conclude that $C_3 = C_4 = 0$. The remaining coefficients C_1 and C_2 are found using the boundary conditions (eq 16). These coefficients are

$$C_1 = \frac{4\pi q k_2^{\,2}}{k_1(k_2^{\,2} - k_1^{\,2})} \qquad \text{(A4)}$$

$$C_2 = \frac{4\pi q k_1^{\,2}}{k_2(k_1^{\,2} - k_2^{\,2})} \qquad \text{(A5)}$$

Hence, the potential $\phi(x)$ is

$$\phi(x) = \frac{4\pi q}{k_2^{\,2} - k_1^{\,2}}\left(\frac{k_2^{\,2}}{k_1} e^{k_1 x} - \frac{k_1^{\,2}}{k_2} e^{k_2 x}\right) \qquad \text{(A6)}$$

For typical high-temperature superconductors, we can prove that $(32\pi e^2/\beta)\xi^2 \gg 1$. Indeed[9]

$$K = \frac{m^* c}{2e\hbar}\left(\frac{\beta}{2\pi}\right)^{1/2} = \frac{137}{2e}\frac{m^* e^2}{\hbar^2}\left(\frac{\beta}{2\pi}\right)^{1/2} \qquad \text{(A7)}$$

where c is the speed of light. Using eq A7,

$$\frac{32\pi e^2}{\beta}\xi^2 = (4.1 \times 10^4)\left(\frac{m^* e^2}{\hbar^2}\right)^2 \frac{\xi_0^{\,2}}{K^2}\left(\frac{T_c}{T_c - T}\right) \gg (4.1 \times 10^4)\left(\frac{m^* e^2}{\hbar^2}\right)^2 \frac{\xi_0^{\,2}}{K^2} \qquad \text{(A8)}$$

For $YBa_2Cu_3O_{7-\delta}$ and $La_{1.8}Sr_{0.2}CuO_4$, $K \approx 100$ and $\xi_0 \approx 2 \times 10^{-7}$ cm.[11] Since $\hbar^2/m^* e^2 \approx 0.53 \times 10^{-8}$ cm,

$$\frac{32\pi e^2}{\beta}\xi^2 > 5.8 \times 10^3 \gg 1 \qquad \text{(A9)}$$

Using inequality A9, we can approximate eq A3 with

$$k_1 = -\xi^{-1/2} e^{i(\pi/4)}\left(\frac{32\pi e^2}{\beta}\right)^{1/4} \qquad \text{(A10)}$$

$$k_2 = -\xi^{-1/2} e^{-i(\pi/4)}\left(\frac{32\pi e^2}{\beta}\right)^{1/4} \qquad \text{(A11)}$$

Substituting eqs A10 and A11 into eq A6 and using eq A7, we obtain the result in eq 20.

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