Attraction Between Electron Pairs in High Temperature Superconductors

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It is proposed that in high temperature superconductors Cooper pairs form and condense due to the monotonic-oscillatory transition in the pair potential of mean force, which occurs quite generally at high coupling in charge systems. It is shown that the predicted transition temperatures are broadly in line with measured superconducting transition temperatures for reasonable values of the total electron density and the residual dielectric permittivity arising from the immobile electrons. The predicted transition is independent of the isotopic masses of the solid. Consequent design principles for high temperature superconductors are discussed.

I. INTRODUCTION

The Bardeen-Cooper-Schrieffer (BCS)\textsuperscript{1,2} theory of superconductivity is based on electron pairs forming zero-momentum, zero-spin bosons bound together by an attractive interaction. For normal low temperature superconductors the accepted mechanism for the attraction is the dynamic interaction of the electron pair with phonons, which are the quantized vibrations of the solid lattice. The dependence of the transition temperature on the isotopic masses of the solid\textsuperscript{1,2,3} confirms BCS theory.

In the late 1980’s high temperature superconductors with transition temperatures above 30 K were discovered\textsuperscript{4–6}. These are independent of the isotopic masses, which rules out the phonon exchange mechanism. New materials with ever higher superconducting transition temperatures have been discovered in the ensuing years, but despite many proposals\textsuperscript{7–12} no consensus has emerged for the nature of the attractive potential that forms Cooper pairs in these materials.

In this paper I propose that the electron attraction responsible for Cooper pairs in high temperature superconductors is due to the oscillatory pair static correlation function that occurs at high coupling. This has long been established for like-charged particles in the one component plasma and in primitive model electrolytes\textsuperscript{13–20}. Here the high-temperature superconductor is modeled as a one-component plasma \textit{in media}, with the relatively few electrons in the Fermi foam comprising the fluid charges, and the fixed nuclei and majority immobile electrons in the Fermi sea forming the neutralizing background and static relative permittivity (dielectric constant). The predicted temperatures for the monotonic-oscillatory transition in this model encompass the measured transition temperatures for high temperature superconductors for physically reasonable values of the total electron density and static relative permittivity.

II. MODEL AND ANALYSIS

The solid conductor is modeled as a one component plasma (mobile electrons in a uniform counter-charge background), together with a finite relative permittivity, \( \epsilon_t = O(10^2) \), that results from the remaining immobile but polarizable electrons (i.e. those deep in the Fermi sea). The mobile electrons at the Fermi foam have number density \( \rho_F(T) \) derived below. Arguments concerning this model are canvassed in the conclusion.

I begin with the restricted primitive model electrolyte for three reasons: First, there are a wealth of analytic, numeric, and experimental results known for electrolytes. Second, it shows the generality of the monotonic-oscillatory transition in charge systems. And third, it gives a specific value for the width of the accessible energy states, which is required to determine the electron density of the Fermi foam.

In the restricted primitive model electrolyte (ions of equal hard sphere diameter), the pair distribution function undergoes an oscillatory transition when\textsuperscript{19}

\[ \kappa_B d \geq \sqrt{2}, \]  

(2.1)

where \( d \) is the hard core diameter of the ions. The inverse Debye screening length for the binary symmetric electrolyte is \( \kappa_D = (4\pi\beta/\epsilon)2\rho_F q^2 \), where \( q \) is the ionic charge (in this case the electron charge), and \( \rho_F \) is the number density of each type of ion. Here \( \beta = 1/k_B T \) is the inverse temperature, and \( \epsilon = 4\pi\epsilon_0\epsilon_\alpha \) is the total permittivity of the medium, \( \epsilon_0 \) being the permittivity of free space (SI units). This result is based on the Debye-Hückel form for the pair distribution function combined with the exact Stillinger-Lovett second moment condition. More accurate analytic and numeric approximations exist\textsuperscript{20} but this is sufficient for the present purposes.

To make the connection with the one component plasma, which does not impose a hard core diameter, the distance of closest approach of the electrons can be set as the point at which the Coulomb potential in \textit{media} reaches several times the thermal energy, \( u(d) = u(k_B T) \), or \( d = \beta\epsilon/\epsilon_\alpha \). With these the oscillatory transition in the symmetric electrolyte occurs when

\[ 2 \leq \frac{4\pi\beta^2\rho_F e^2}{\epsilon} \frac{\beta^2 e^4}{\epsilon^2 \alpha^2} = \frac{6}{\alpha^2} \frac{\epsilon}{\epsilon_\alpha} \frac{\beta^2}{\epsilon_\alpha}. \]  

(2.2)

Here the plasma coupling parameter with finite relative permittivity is \( \Gamma \equiv \beta^2/\epsilon(3/4\pi\rho_F)^{1/3} \).

As mentioned, the parameter \( \alpha \) is the multiple of the thermal energy which bounds the accessible states.

\[ \rho_F = \frac{1}{\sqrt{2\pi}} \frac{\pi^2}{\alpha^3} \frac{\epsilon}{\epsilon_\alpha} \left[ \epsilon - \frac{\beta^2}{\epsilon_\alpha} \right]. \]  

(2.3)
Choosing $\alpha = \sqrt{24} \approx 4.9$, the transition criterion becomes

$$\Gamma \geq 2. \quad (2.3)$$

With this value of $\alpha$, the value of the coupling constant at the transition given for the restricted primitive model electrolyte agrees with that found by Monte Carlo simulations of the one component plasma.\(^{14}\)

I now estimate the density of the electrons in the Fermi foam modeling them as a non-interacting ideal gas, also known as the free electron model. The Fermi momentum and the Fermi energy for ideal fermions are\(^{21}\)

$$p_F = 2\pi \hbar \left( \frac{3\rho}{8\pi} \right)^{1/3}, \quad \text{and} \quad \epsilon_F = \frac{(2\pi\hbar)^2}{2m} \left( \frac{3\rho}{8\pi} \right)^{2/3}, \quad (2.4)$$

where $\rho = N/V$ is the total electron number density. The thermal wavelength is $\Lambda = \sqrt{2\pi\beta\hbar^2/m}$, and $\beta\epsilon_F = 2\pi(3\rho\Lambda^3/8\pi)^{2/3}/2$, which is much larger than unity.

With momentum state spacing being $\Delta_p = 2\pi\hbar/L^{22\text{ to} 23}$ where the volume is $V = L^3$, the number in the Fermi foam is

$$N_F = 2\Delta_p^{-3} \int_{\epsilon_F - \alpha/\beta}^{\epsilon_F + \alpha/\beta} d\epsilon 4\pi m \sqrt{2m\epsilon} \frac{e^{-\beta(\epsilon - \epsilon_F)}}{1 + e^{-\beta(\epsilon - \epsilon_F)}} \approx 4\alpha N\Lambda^{-3}(3\rho\Lambda^3/8\pi)^{1/3}. \quad (2.5)$$

An expansion to leading order for large $\beta\epsilon_F$ has been made to obtain the final equality. That is

$$\rho F \Lambda^3 = 4\alpha \left( \frac{3\rho\Lambda^3}{8\pi} \right)^{1/3}. \quad (2.6)$$

The total excitonic electron density, $\rho_F$, is significantly less than the total electron density, $\rho$. It is proportional to the number of accessible energy states at the Fermi energy, which is fixed by equating the results of the restricted primitive model to those of the one component plasma, $\alpha = \sqrt{24}$.

The idea that only the electrons at the Fermi surface contribute to screening also underlies the Thomas-Fermi model of the electron gas.\(^{24}\) This idea is taken a little further here by modeling the remaining immobile electrons as being polarisable and contributing to the residual dielectric constant.

### III. NUMERICAL RESULTS

The predicted oscillatory-monotonic transition temperature is now explored for a range of the two free parameters: the total electron density $\rho$ and the residual static relative permittivity $\epsilon_r$. For these a guide is provided by values for ceramic materials. The total electron density of zirconia $\text{ZrO}_2$ is $\rho = 1.65 \times 10^{29}$ m$^{-3}$. The relative permittivity of typical ceramic insulators is on the order of $\epsilon_r = 10^1$–$10^2$.\(^{25}\)

![FIG. 1: Coion pair potential of mean force as a function of separation in the symmetric binary monovalent electrolyte ($d = 3.41$ Å, $\epsilon_r = 100$, $T = 100$ K, hypernetted chain approximation). The solid curve is $0.5 \text{ M}$, ($\alpha d^2 = 1.5$, $\Gamma = 1.8$), the short-dash curve is $1.0 \text{ M}$, ($\alpha d^2 = 2.9$, $\Gamma = 2.3$), the long-dash curve is for $2.0 \text{ M}$ ($\alpha d^2 = 5.9$, $\Gamma = 2.9$). The solid line is an eye guide.](image)
and \( \rho \) the transition to oscillatory behavior. In all cases \( \alpha \) are greater than those measured for high temperature superconductors.

Figure 3 shows the transition temperature as a function of the relative permittivity. From left to right the curves are for a total electron density of \( \rho = 0.1, 1, \) and \( 10 \times 10^{30} \text{ m}^{-3} \).

**IV. CONCLUSION**

Perhaps the most controversial aspect of the proposed model is the invocation of a finite relative permittivity for the solid. The perceived wisdom is that a conductor has infinite permittivity. Also, the one component plasma is usually modeled in vacuo, \( \epsilon_r = 1 \). In response to these anticipated objections I make the following points. First, one has to distinguish between an experimental challenge and a fundamental limitation of nature. There is no doubt that a macroscopic measurement of the dielectric constant of a conductor yields an infinite dielectric constant in the zero frequency limit. In my opinion, all this says is that the conductivity dominates the measurement; it does not say that the residual relative permittivity is either unity or infinity. Second, fixed atoms surrounded by the electrons deep in the Fermi sea, which include the immobile inner shell electrons, remain polarizable, and therefore they must contribute to a finite relative permittivity. Third, if the relative permittivity were truly infinite at the molecular level, then the immobile electrons could not interact via the Coulomb repulsion, and they would be utterly transparent to each other, which is obvious nonsense. Fourth, and finally, insulators that are close in chemical composition and physical structure to specific high temperature superconductors, have a measured finite relative permittivity greater than unity. For example, cuprate superconductors are insulators if the doping fraction is less than 0.1 holes per CuO

FIG. 2: Plasma coupling parameter in media using electron density \( \rho_p(T), \) Eq. (2.6), and, from bottom to top, relative permittivity \( \epsilon_r = 200, 150, 100, \) and 75. The dotted line marks the transition to oscillatory behavior. In all cases \( \alpha \) = \( \sqrt{24} \) and \( \rho = 10^{30} \text{ m}^{-3} \).

FIG. 3: Transition temperature as a function of the relative permittivity. From left to right the curves are for a total electron density of \( \rho = 0.1, 1, \) and \( 10 \times 10^{30} \text{ m}^{-3} \).
hand, the quantitative prediction of the transition temperature and the depth of the primary minimum cannot be taken too literally for electrons in the layered crystalline solids that are of interest in high temperature superconductivity.

This paper proposes that the oscillatory potential of mean force that occurs at high coupling is responsible for Cooper pair formation and superconductivity. The BCS theory is predicated upon an attractive potential, not an attractive potential of mean force. The difference between the pair potential and the pair potential of mean force is fundamentally the difference between quantum mechanics and quantum statistical mechanics. It is the latter, not the former, that is the appropriate theory for condensed matter. In an accompanying paper I give a new quantum statistical mechanical theory for superconductivity that shows explicitly how Cooper pairs form and condense depending upon the potential of mean force.28 The theory uses the classical phase space formulation of quantum statistical mechanics,29 30 together with techniques recently developed for superfluidity.31 32

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