Theory of fluctuation superconductivity from electron-phonon interactions in pseudo-one-dimensional systems*

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The physics of quasi-one-dimensional solids which undergo a Peierls distortion, such as the organic material TTF-TCNQ (tetrathiofulvalinium-tetracyanoquinodimethan) is discussed. In particular, the effect of fluctuations into the Fröhlich superconducting state on the free energy and the electrical conductivity is examined theoretically at temperatures above that of the Peierls distortion. A phenomenological approach is used, but the physical basis for a microscopic treatment is given and the results are compared with the effect of fluctuations into a BCS superconducting state. It is found that such fluctuations give a paraconductivity which is too small to account for the extraordinary conductivity peaks reported for TTF-TCNQ.

I. INTRODUCTION

There has been considerable interest in the possibility of superconductivity in pseudo-one-dimensional organic solids following a suggestion by Little.[1] Recently, Coleman *et al.*[2] reported high electrical conductivity just above the Peierls soft-mode instability in an organic system. The high conductivity was observed using a four-probe method in three single crystals of TTF-TCNQ (tetrathiofulvalinium-tetracyanoquinodimethan) out of 70 and in polycrystalline specimens of a closely related compound, ATTF-TCNQ (asymmetric-TTF-TCNQ). They attempted to account for the results in terms of fluctuation superconductivity, usually called paraconductivity, resulting from a BCS-type pairing just above the transition temperature T_c. Below T_c, the materials exhibit a semiconducting or insulating behavior. One of the authors of the present paper suggested[3] that the paraconductivity is more likely described by an earlier theory of Fröhlich,[4] who showed that superconductivity in one-dimensional systems might result from a coupling between the electrons and a traveling macroscopically occupied lattice wave. This concept is further developed in the present paper, and we find that the model, at least in its simplest form, gives a paraconductivity that is too small to account for the results.

Fröhlich's theory was based on a nearly-free-electron model and applied only to $T=0$ °K. As a result of electron-phonon coupling, a macroscopic energy gap opens up at the Fermi surface (the Peierls transition). Fröhlich suggested that if, when the electrons are displaced in k space so as to give a current flow, the gaps follow the displaced Fermi surface, superconductive behavior might result. The theory was extended to higher temperatures by Kuper,[5] who calculated the behavior near the transition temperature T_c, but only for zero current flow.

A tight-binding model is more appropriate to the organic conductors. We have extended Fröhlich's theory to apply to the case of tight binding and have made a mean-field estimate of the paraconductivity above T_c, although we do not yet have a complete microscopic theory. It turns out that, although the physics is quite different, Fröhlich's model gives some mathematical results very similar to those of the BCS theory. However, Patton and Sham[6] have shown from a diagrammatic approach that in the Fröhlich model there are two conductivity diagrams analogous to the Aslamazov-Larkin[7] diagram that give equal and opposite contributions to the paraconductivity, and so give a null result. (See note added in proof.) Further they have shown that diagrams analogous to the Maki[8] diagrams give a negative contribution to the paraconductivity.

As shown by Rice and Strässler[9] and Patton and Sham,[6] soft modes cannot account for superconducting behavior in materials with such a high T_c. According to the BCS and Eliashberg[10] theories based on pairing, modes with frequencies below the gap (or $k_B T_c$) give a repulsive rather than an attractive interaction. Gutfreund, Horovitz, and Weger[11] have suggested a pairing theory based on high-frequency optical phonons. This is a possible explanation, but according to them, it is just a coincidence that the superconducting transition temperature is close to the Peierls transition temperature.

Bychkov, Gor'kov, and Dzyaloshinskii[12] have shown that a BCS pairing resulting from a net attractive interaction between electrons combines with the Peierls instability from a lattice deformation to give a single transition in which both effects contribute to the energy gap. A theory of this sort may be the correct one. However, it appears likely that the gap comes mainly from a lattice deformation, and in this case superconducting effects from pairing are greatly reduced.

Actually, because of fluctuations, one cannot

have a phase transition in a one-dimensional model. The observed transition takes place in three dimensions, reflecting at least a weak interaction between parallel chains of TCNQ molecules, perhaps via the cations. As Lee, Rice, and Anderson[13] have pointed out, the actual transition temperature T_c may be reduced considerably below that given by mean-field theory for a single chain. Our calculations are based on mean-field theory and may underestimate fluctuation effects.

The main purpose of the present paper is to discuss the physics of Fröhlich's model, in particular as it applies to paraconductivity. It is hoped that it may serve as the basis for a more complete microscopic theory.

In a superfluid there must be a macroscopic occupation of a quantum state that picks out a unique reference frame which describes the velocity, v_s, of the superfluid. Associated with each value of v_s, there is a whole set of elementary excitations of the system. If, when excitations come into equilibrium with the rest frame, a current $J_s(v_s)$ remains, the system is a superfluid with a superfluid velocity v_s. In superfluid helium, there is a macroscopic occupation in the Bose condensate of the momentum state $p_s = mv_s$. In a superconductor based on pairing, it is the common momentum of the pairs that defines v_s. In the Fröhlich model there is no pairing and no Bose condensation; v_s is determined by the velocity of the macroscopically occupied lattice wave which produces energy gaps at the boundaries of the displaced Fermi surface. In calculating the various thermodynamic quantities, including supercurrent flow, v_s is treated as a fixed macroscopic variable of the system. It is possible that v_s may vary slowly in space.

The total momentum, which includes the crystal momentum of the lattice waves, is considerably larger than that of the electrons and may be expressed, following Fröhlich, as

$$P = P_e + P_L = n_s(m^* + m_1)v_s\,, \tag{1.1}$$

where m^* is the effective mass of the electrons and $m_1 \gg m^*$ is related to the momentum in the lattice waves. Such states may decay by umklapp processes in which an electron may be scattered from one side of the Fermi distribution to the other by a lattice wave of small wave vector q,

$$k \rightarrow k' \pm q + G\,, \tag{1.2}$$

where G is a reciprocal-lattice vector. Thus below T_c the only stable state is that with $v_s = 0$. This is a true insulating state; when an electric field is applied v_s remains equal to zero. However, if the relaxation times for umklapp processes are sufficiently long, one could have fluctuation modes with finite lifetime existing above T_c. We assume this to be the case.

In a true superfluid, states with $v_s \neq 0$ are metastable and can exist for a very long time. This is because a large momentum is required to change v_s, and scattering of individual particles of the system does not give a momentum change sufficient to change the value of v_s. In a one-dimensional system, the momentum associated with v_s is not sufficiently large, and the decay to $v_s = 0$ may be fairly rapid. This apparently happens in the systems studied by Coleman *et al.*

In Fröhlich's theory, one starts with a Hamiltonian which includes interactions between the electrons and phonons, but direct Coulomb interaction between electrons is neglected completely. The main virtue of the TCNQ materials is that the extra Coulomb energy is small when there are two extra electrons on the TCNQ molecule, making the free radical $(TCNQ)^{--}$. This is helped by the juxtaposition of the highly polarizable cations TTF or ATTF. If the Coulomb energy is less than the bandwidth of the tight-binding band for conduction along the $(TCNQ)^-$ chains, it may be neglected in first approximation and may be treated in higher approximation by perturbation theory if so desired.

The crystal structure of $(TTF)^+$ $(TCNQ)^-$ has been determined recently by Phillips *et al.*[14] using x-ray-diffraction methods. They find that "the structure is made up of *segregated* columnar stacks of radical cations $(\cdots D^+D^+D^+D^+\cdots)$ and radical anions $(\cdots A^-A^-A^-A^-\cdots)$." It is not certain whether or not there is transfer of a full electron from the cation to the anion, although we shall assume for simplicity that this is the case.

We take for our model a simple one-dimensional chain of molecules, with a spacing $d \simeq 3.8$ Å and one extra electron per molecule. Above T_c the spacing between molecules is equal so that the tight-binding band extending in k space from $-\pi/d$ to $+\pi/d$ has room for two electrons per molecule. Since we assume one, the band is half-filled. This makes the mathematics a little simpler, since there is symmetry between electrons and holes, but it is not essential to the theory.

There is still some uncertainty in regard to the experimental results. The extraordinary conductivity was observed in TTF-TCNQ in only three out of some 70 crystals measured. Consistent results were obtained with ATTF-TCNQ, but it has not been possible so far to make single crystals, necessitating the use of silver paint to short out the high resistance between grains. Conductivity measurements by a four-probe method in highly anisotropic systems can be misleading. Bloch *et al.*,[15] working at Johns Hopkins, found no anomalous conductivity associated with fluctuation superconductivity at microwave frequencies in either TTF-TCNQ or ATTF-TCNQ, but it is not certain that

the samples measured by the Johns Hopkins group were of equivalent quality to those measured by the Pennsylvania group. Chaikin *et al.*[16] note that the tendency of the thermopower to go to zero at T_c, which they have observed, is consistent with the appearance of superconducting fluctuations just above T_c.

Independently of the work on these organic systems, Rice and Strässler[17] have worked out the theory for the Peierls instability in one-dimensional systems for application to systems such as $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$ (KPC), in which above T_c there is conduction along chains of Pt ions. The bromine ions take electrons from the platinum, leaving a partially filled tight-binding band with hole conduction. Below T_c, there is a Peierls transition to an insulating phase. Although they do not consider current-carrying states with $v_s \neq 0$, they show the close connection between the Peierls instability in which gaps appear at the Fermi surface and the BCS theory. They also start from the Fröhlich Hamiltonian in which Coulomb interactions are neglected.

The basis for Fröhlich's theory as applied to a half-filled tight-binding band is shown in Fig. 1. It is assumed that on the average there is one electron per molecule with spacing d so that the energy as a function of wave vector k measured from the Fermi energy is

$$\epsilon(k) = -E_F \cos(kd) , \tag{1.3}$$

where $k_F = \pi/2d$ for a half-filled band. When $v_s = 0$, the Peierls instability gives a distortion of period $2d$ with energy gaps of magnitude $2\Delta_0$ at $k_F = \pi/2d$, the boundaries of the occupied states at $T = 0\ ^\circ\mathrm{K}$, as shown in Fig. 1(a). If only the states below the gap are occupied, there will be a lowering of electron energy at the expense of the energy required to distort the lattice.

If there is a current flow with velocity v_s, the electrons are displaced in k space as shown in Fig. 1(b). In tight binding, if the electrons are displaced by q with $q \ll k_F$, we may define v_s by

$$m^* v_s = \hbar q , \tag{1.4}$$

with

$$m^* v_F = \hbar k_F \tag{1.5}$$

and

$$\hbar v_F = \left(\frac{d\epsilon}{dk}\right)_{k=k_F} = E_F d ; \tag{1.6}$$

thus

$$m^* = \hbar^2 k_F / E_F d = 2\hbar^2 k_F^2/(\pi E_F) . \tag{1.7}$$

The displaced Fermi distribution extends from $-k_F + q$ to $k_F + q$. If the energy gaps follow the Fermi distribution, the energies of the electrons will be as shown in Fig. 1(b). If $\hbar k_F v_s < \Delta$, only the states below the gap will be occupied and the current flow will be nev_s. Thus at $T = 0\ ^\circ\mathrm{K}$, $n_s = n$. As the temperature is raised, electrons will be scattered back to the next higher band to decrease the current. Thus n_s will decrease, approaching zero as $T \to T_c$.

A macroscopic travelling lattice wave is required to give the gaps at the two sides of the displaced Fermi distribution. The wave should have Fourier components $\exp[i2k_F(x - v_s t)]$, or a wave vector $2k_F$ and frequency $\omega = 2k_F v_s$. The energy $\hbar\omega$ just corresponds to the energy difference between the opposite sides of the displaced Fermi surface. For simplicity, we shall assume that the matrix elements of the lattice-wave potential between the states k and $k - 2k_F$ are independent of k. If one goes to a reference frame moving with the electrons with velocity v_s relative to the lattice frame, the energy gap will be the same as for $v_s = 0$, except for the fact that excitations from the ground state should come into equilibrium with

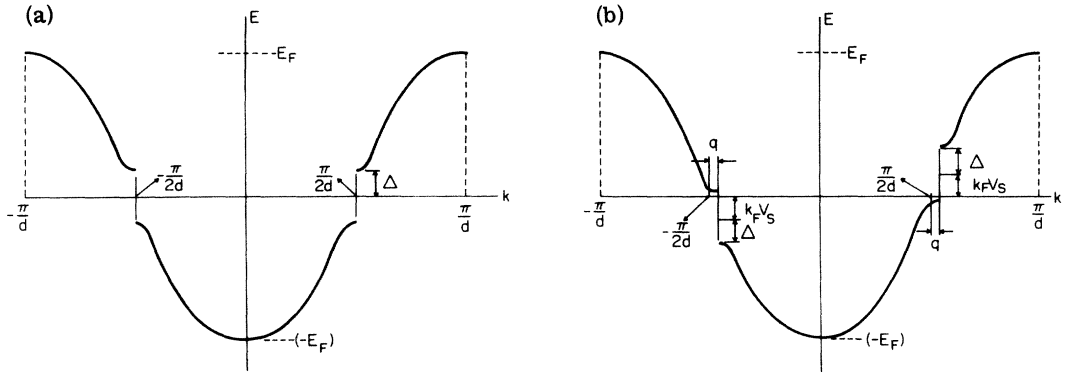

FIG. 1. (a) The half-filled tight-binding band which has undergone a Peierls transition. There is no current ($v_s = 0$), and the gaps are exaggerated for clarity. (b) Same as (a) except $v_s \neq 0$.

the lattice moving at a relative velocity $-v_s$.

There is a problem with an exactly-half-filled tight-binding band which is believed to be more formal than real. In this case, $2k_F$ is associated with a periodicity of $2d$, which corresponds to every other molecule vibrating in phase with frequency ω. This represents a standing wave rather than the running wave we require. This difficulty is not encountered if $2k_F$ departs slightly from π/d. This case is discussed in Appendix A.

Actually, we make no explicit use of a half-filled band except for assuming equivalence between electrons and holes, and this will be true to a good approximation in any case in the vicinity of the Fermi energy as long as $k_B T \ll E_F$, as is true in most cases. Since fluctuation conductivity depends only on such excitations, the results should be valid in general. Use of mean-field theory is not justified for one-dimensional systems, so that our results cannot be expected to be valid except as to order of magnitude.

In Sec. II we review the theory of the Peierls transition for $v_s = 0$ and show that the expression for the free energy near T_c is very similar to that given by the usual Ginzburg-Landau theory. In tight binding, the gap parameter Δ_0 at $T = 0\ ^\circ\mathrm{K}$ is

$$\Delta_0 = 4E_F\, e^{-1/\lambda}\ , \tag{1.8}$$

where λ is the electron-phonon interaction parameter. Note that the Fermi energy appears in place of the phonon-energy cutoff of the BCS theory, giving the possibility of a high transition temperature. The relation between T_c and Δ_0 is exactly the same as in the BCS theory:

$$k_B T_c = 0.57\Delta_0\ . \tag{1.9}$$

In Sec. III we show how the results are modified if the gaps follow the displaced Fermi distribution so as to give a current flow. Again, the Ginzburg-Landau result near T_c is very similar to BCS for $v_s \neq 0$, with extra terms coming from the kinetic energy of the supercurrent and the lattice waves. It is likely that for one-dimensional systems these states are not metastable but decay rapidly to the insulating state corresponding to $v_s = 0$.

Section IV is concerned with the calculation of the propagator for the lattice waves, $D(2k_F, \omega)$, in the neighborhood of T_c. Just above T_c, the collective modes corresponding to decaying moving lattice waves for various values of v_s have relatively long lifetimes and contribute to the paraconductivity. Expressions for these lifetimes and for the Ginzburg-Landau free energy are derived.

Finally, in Sec. V an estimate is given of the paraconductivity based on mean-field theory and semiphenomenological arguments. We do not yet have a complete microscopic theory so that the results must be treated with some reservations. An estimate of the validity of mean-field theory is given.

II. PEIERLS DISTORTION

In this section we give a brief review of the physics of the Peierls phase transition applied to one-dimensional tight-binding systems. The quantities of interest that we shall discuss are the temperature at which the transition occurs T_c, the size of the resulting energy gap in the band structure at $T = 0$, $2\Delta_0$, and the free energy of the system as a function of the energy gap and temperature, $F(\Delta, T)$. We consider in this section only the case of no current flow (i.e., $v_s = 0$). The theory as presented here is essentially equivalent to that of Rice and Strässler.[17]

We begin with the Hamiltonian for the quasi-one-dimensional linear chain of length L consisting of n atoms or molecules. We include the electron-phonon interaction, but neglect the Coulomb and phonon-induced interaction between electrons:

$$H = H_e + H_p + H_{e\text{-}p}\ . \tag{2.1}$$

The electron part of H is given by

$$H_e = \sum_k \epsilon(k) a_k^\dagger a_k\ , \tag{2.2}$$

where $\epsilon(k)$ is the tight-binding energy of Eq. (1.3), which may include the self-energy from the phonons. Here $a_k^\dagger$ (a_k) creates (destroys) an electron in state k. The index k includes both wave number and spin. Similarly, the phonon part is

$$H_p = \sum_k \hbar\omega_k b_k^\dagger b_k\ , \tag{2.3}$$

where ω_k in the Debye model is $\hbar\omega_k = ks$ for the velocity of sound s, and $b_k^\dagger$ and b_k are the usual phonon creation and destruction operators. Last, the electron-phonon part is assumed to be

$$H_{e\text{-}p} = \sum_{pk} g(k) a_{p+k}^\dagger a_p (b_k + b_{-k}^\dagger)\ , \tag{2.4a}$$

where $g(k)$ is the electron-phonon coupling constant. An equivalent form of $H_{e\text{-}p}$ expressed in terms of electron wave field operators is

$$H_{e\text{-}p} = \sum_k \int dx\, g(k)(b_k + b_{-k}^\dagger)\, e^{ikx}\, \psi^\dagger(x)\psi(x)\ . \tag{2.4b}$$

However, as discussed by Peierls, Fröhlich,[4] and Kuper,[5] for $T < T_c$ the phonon modes of wave numbers $\pm 2k_F$ which connect the two points of the Fermi surface become macroscopically occupied. For the special case of a half-filled band, the lattice undergoes a distortion in which the period of the lattice doubles. This case is discussed in Appendix A. In general, the order parameter Δ that describes the distortion is defined by

$$\Delta \equiv g(2k_F)\langle b_{2k_F} + b_{-2k_F}^\dagger \rangle\, e^{i2k_F x}\ , \tag{2.5}$$

where the angular brackets denote a thermal average. The equilibrium value of Δ is 0 for $T > T_c$, and there is macroscopic occupation of the $\pm 2k_F$ states for $T < T_c$. An energy gap, $2|\Delta|$, is introduced in the electron band structure so that the one-electron energies become

$$E(k) = \mathrm{sgn}[\epsilon(k)][\epsilon^2(k) + |\Delta|^2]^{1/2} , \tag{2.6}$$

with

$$\mathrm{sgn}[\epsilon(k)] = + \text{ for } \epsilon(k) > 0$$
$$= - \text{ for } \epsilon(k) < 0 .$$

Rice and Strässler have shown that in the tight-binding approximation

$$k_B T_c = 2.28 E_F e^{-1/\lambda} \tag{2.7}$$

and

$$\Delta(T=0) = \Delta_0 = 4E_F e^{-1/\lambda} , \tag{2.8}$$

where k_B is Boltzmann's constant, and λ is given by

$$\lambda = 2N(0)|g(2k_F)|^2/\hbar\omega_{2k_F} ,$$

with $N(0) = n/\pi E_F$.

We now turn to the free energy of the one-dimensional chain, which is assumed to be of the form

$$F(\Delta, T) = -(2/\beta)\sum_k \ln\{2\cosh[\tfrac{1}{2}\beta E(k)]\} + N(0)|\Delta|^2/\lambda , \tag{2.9}$$

where $\beta \equiv (k_B T)^{-1}$. The first term is the usual free energy of a gas of fermions with energies $E(k)$ given by Eq. (2.6). The spin sum has been done, and it accounts for the factor of 2 preceding the summation symbol. The last term is the energy that is required to distort the lattice. There is an additional term when $v_s \neq 0$ which represents the kinetic energy of the moving lattice wave. We point out that the form of Eq. (2.9) is formally identical to that for a BCS superconductor, but the physics underlying the second term and the significance of Δ are different.

To obtain an expression for $F(\Delta, T)$ in the region near T_c where $|\Delta|$ is small, we expand (2.9) in powers of $|\Delta|^2$:

$$F(\Delta, T) - F(0, T) = a|\Delta|^2 + (\tfrac{1}{2}b)|\Delta|^4 + \cdots . \tag{2.10}$$

The coefficients a and b are calculated in Appendix B and are found to be, for T near T_c,

$$a \simeq -N(0)\ln(T_c/T) \simeq -N(0)(T_c - T)/T_c \tag{2.11}$$

and

$$b \simeq 0.106\, N(0)/(k_B T_c)^2 . \tag{2.12}$$

These values are nearly identical with the BCS case.

III. ELECTRON FREE ENERGY ASSOCIATED WITH MOVING LATTICE WAVES

As suggested by Fröhlich and illustrated in Fig. 1, there can be states with current flow if the energy gaps are displaced with the electrons and remain attached to the Fermi surface. This requires that the phase of the order parameter Δ vary in time as well as in space. We shall ignore fluctuations in electron density so that the lattice wave which connects opposite sides of the Fermi distribution and is macroscopically occupied will have a wave vector $2k_F$. If the lattice wave moves with the electrons with velocity v_s, the order parameter will vary as

$$\Delta = |\Delta| e^{2ik_F(x - v_s t)} . \tag{3.1}$$

Note that v_s is related to the frequency and thus to the time derivative of the phase.

We shall assume that $|\Delta| \ll E_F$, so that we can ignore the differences between the gaps on the right- and left-hand sides of the one-dimensional Fermi distribution. For energies small compared with E_F, the excitation energies are of exactly the same form as for a BCS superconductor in which the momentum of the pairs is $2p_s = 2m^* v_s$. As we have seen, expressions for the Ginzburg-Landau free-energy functional are nearly identical and differ mainly in the term associated with the kinetic energy of the moving lattice wave.

If the electrons in the ground state are displaced by a wave vector q, it is convenient to measure k from the displaced origin q so that the Fermi surface remains at $\pm k_F$, with k_F a positive number. Near the Fermi surface, the energies are given by

$$E(k) = \mathrm{sgn}(\epsilon_k)(\epsilon_k^2 + |\Delta|^2)^{1/2} \pm \hbar k_F v_s , \tag{3.2}$$

where the ϵ_k are the energies relative to the Fermi surface of the undisplaced distribution with $\Delta = 0$. The positive sign refers to the right and the negative sign to the left. Note that the frequency factor in Δ, $\omega = 2k_F v_s$, just makes up for the difference in energies between the left- and right-hand sides of the displaced distribution, so that the expression for the gap as derived from the matrix elements of the potential of the lattice wave is essentially the same as for $v_s = 0$. There is a slight difference for energies near the top and bottom of the band, but these have a very small effect if $|\Delta| \ll E_F$ and v_s is small. At $T = 0\,^\circ\mathrm{K}$, the current density for $\hbar k_F v_s < \Delta_0$ is proportional to

$$\int_{-k_F}^{k_F} \frac{\partial E}{\partial k} dk = E(k_F) - E(-k_F) , \tag{3.3}$$

and is the same as that for $\Delta = 0$. The mass flow is $nm^* v_s$ so that $n_s = n$. When $\hbar k_F v_s$ becomes greater than $|\Delta|$, electrons can be scattered back to the next higher band and the current will decrease

rapidly to zero, as in a pairing superconductor. This gives an effective upper limit on v_s.

Near T_c, one may expand the free-energy functional (2.9) in powers of $|\Delta|^2$ and v_s^2 and obtain to order of v_s^2:

$$F = F_s - F_n = a|\Delta|^2 + \tfrac{1}{2}b|\Delta|^4 + \tfrac{1}{2}cnm^*v_s^2|\Delta|^2 , \tag{3.4}$$

where a and b are given by (2.11) and (2.12) and c is identical with the value for a pairing superconductor:

$$c = 7\zeta(3)/4\pi^2(k_B T_c)^2 . \tag{3.5}$$

The mass flow of the electrons is to first order in v_s,

$$P_e \equiv n_s m^* v_s = cnm^* v_s |\Delta|^2 ; \tag{3.6}$$

thus

$$n_s/n = c|\Delta|^2 . \tag{3.7}$$

If we use $m^*v_s = \hbar q$, the terms in $|\Delta|^2$ may be written in the form

$$a(1 + \xi^2 q^2)|\Delta|^2 , \tag{3.8}$$

where

$$\xi^2 \equiv \hbar^2 cn/2m^*|a| \tag{3.9}$$

defines the Ginzburg-Landau coherence length, approximately equal to

$$\xi^2 \simeq \xi_0^2/\epsilon , \tag{3.10}$$

where ξ_0 is the temperature-independent coherence distance and $\epsilon = |T - T_c|/T_c$. In our case v_s is related to the frequency or time derivative of the phase of the order parameter, not to the space gradient. There is an additional term of order v_s^2 from the lattice kinetic energy which may be incorporated in ξ^2 by adding a factor $(1 + m_1/m^*)$ as discussed in Sec. IV.

Because of umklapp processes in pure one-dimensional materials and scattering by imperfections, the states for a given v_s are not metastable but will decay with some relaxation time τ to the equilibrium state $v_s = 0$. For the states defined by v_s to make sense, one should have $\omega\tau = 2k_F v_s \tau > 1$.

To observe true superconductivity there would have to be coherence between parallel chains, which is unlikely for $v_s \neq 0$ unless there is an attractive interaction as in a pairing superconductor. There could then be a reasonable coherence distance transverse to the chains and a large amount of momentum associated with v_s. In this case v_s could not be changed by scattering by imperfections, and it would require a macroscopic disturbance such as passages of a vortex line to change the current.

However, in the absence of true superconductivity, it may be possible to observe fluctuation superconductivity above T_c. In Sec. IV we discuss the propagator for the lattice wave and derive the kinetic energy associated with the moving lattice wave.

IV. $2k_F$-PHONON PROPAGATOR

The value for the decay time of the fluctuations that contribute to the electrical conductivity for $T > T_c$ and the term in the free energy due to the kinetic energy of the moving lattice waves may both be obtained from the propagator of the $2k_F$ phonon. We assume that the softening of the phonon mode is sufficiently sharp that we may neglect any deviation of phonon wave vector from the $2k_F$ value. Then, since the $2k_F$-phonon propagator is formally analogous to the t matrix of the usual pairing superconductivity theory, the poles of the propagator may be examined to find the real and imaginary parts of the frequency of the excitation and also the Ginzburg-Landau free energy of the system.

In order to do a complete microscopic calculation, one would need to obtain the total phonon propagator $D(2k_F, \omega)$. Following Patton and Sham,[6] we shall here consider only the electron-hole bubble self-energy terms. The diagram expansion for $D(2k_F, i\omega_n)$ is given in Fig. 2. We shall use the standard technique of evaluating the equation for D at the imaginary Matsubara frequencies and then analytically continuing to the real frequencies ($i\omega_n \to \omega + i\delta$ for δ a positive infinitesimal) to obtain the physical causal behavior.

The Dyson equation for D is thus seen to be

$$D^{-1}(2k_F, i\omega_n) = D_0^{-1}(2k_F, i\omega_n) - [\lambda/N(0)\beta] \times \sum_{m,p} G^0(p, i\omega_m) G^0(p - 2k_F, i(\omega_m - \omega_n)) , \tag{4.1}$$

where

$$D_0(2k_F, i\omega_n) = \omega_{2k_F}^2 [(i\omega_n)^2 - \omega_{2k_F}^2]^{-1} \tag{4.2}$$

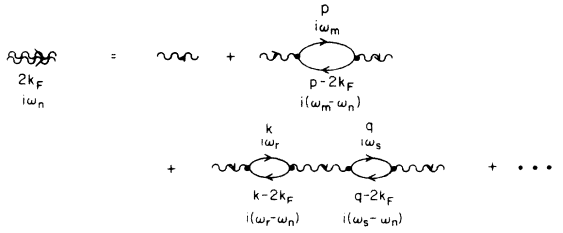

FIG. 2. Diagram expansion for the $2k_F$-phonon propagator, $D(2k_F, i\omega_n)$. A double wiggle denotes the phonon propagator including the self-energy corrections, a single wiggle stands for the zero-order phonon propagator having momentum $2k_F$ and frequency $i\omega_n$, and a line represents the zero-order electron propagator. A dot denotes the electron-phonon vertex and contributes a factor $i\tilde{g} = ig_{2k_F}(2/\omega_{2k_F})^{1/2}$.

and

$$G^0(p,i\omega_n)=[i\hbar\omega_n-\epsilon(p)]^{-1}\ . \tag{4.3}$$

As usual, the Matsubara frequencies are $\hbar\omega_n=2\pi n/\beta$ and $\hbar\omega_m=(2m+1)\pi/\beta$, where n and m are integers.

From the periodicity of the tight-binding band structure, we have

$$\epsilon(p-2k_F)=-\epsilon(p)$$

and hence

$$G^0(p-2k_F,i(\omega_m-\omega_n))=-G^0(p,i(\omega_n-\omega_m))\ .$$

Equation (4.1) then becomes

$$D^{-1}(2k_F,i\omega_n)=D_0^{-1}(2k_F,i\omega_n)+(\lambda/N(0)\beta)\times\sum_{m,p}G^0(p,i\omega_m)G^0(p,i(\omega_n-\omega_m))\ . \tag{4.4}$$

Inserting the expression for D_0^{-1}, doing the frequency sum, and setting

$$\sum_p\rightarrow N(0)\int_{-E_F}^{E_F}\frac{d\epsilon}{(1-\epsilon^2/E_F^2)^{1/2}}$$

results in

$$\omega_{2k_F}^2D^{-1}(2k_F,i\omega_n)=(i\omega_n)^2-\omega_{2k_F}^2\times\left(1+\lambda\int_{-E_F}^{E_F}\frac{d\epsilon}{(1-\epsilon^2/E_F^2)^{1/2}}\,\frac{\tanh\frac{1}{2}\beta\epsilon}{i\hbar\omega_n-2\epsilon}\right). \tag{4.5}$$

Using Eqs. (B4) and (B7) from Appendix B, we have the relation

$$1=\lambda\ln(T/T_c)+\lambda\int_{-E_F}^{E_F}\frac{d\epsilon}{2\epsilon(1-\epsilon^2/E_F^2)^{1/2}}\tanh\tfrac{1}{2}\beta\epsilon\ . \tag{4.6}$$

This reduces (4.5) to the following form after performing the analytic continuation to the real ω axis, $i\omega_n\rightarrow\omega+i\delta$:

$$\omega_{2k_F}^2D^{-1}(2k_F,\omega)=\omega^2-\omega_{2k_F}^2\lambda\left[\ln\frac{T}{T_c}+\int_{-E_F}^{E_F}\frac{d\epsilon}{(1-\epsilon^2/E_F^2)^{1/2}}\tanh\tfrac{1}{2}\beta\epsilon\times\left(\frac{1}{2\epsilon}-\frac{1}{2\epsilon-\hbar\omega-i\delta}\right)\right]. \tag{4.7}$$

The integral is evaluated by again using the cutoff X such that $2/\beta\ll X\ll E_F$ and expanding in powers of ω. To order ω^2 the result is

$$D^{-1}(2k_F,\omega)=-\lambda\{-\omega^2/\lambda\omega_{2k_F}^2+\ln(T/T_c)-\tfrac{1}{8}i\pi\beta_c\hbar\omega+\tfrac{1}{16}[7\zeta(3)(\hbar\omega\beta_c/\pi)^2]\}\ , \tag{4.8}$$

where we have dropped a term proportional to ω^2/E_F^2 since it is much smaller than the term $\omega^2\beta_c^2$.

Equation (4.8) gives the value of the inverse of the $2k_F$-phonon propagator for real values of the frequency ω. The poles of $D(2k_F,\omega)$ are given by $D^{-1}(2k_F,\omega=\omega')=0$, where we have continued into the complex ω plane.

In Sec. III we found that $|\Delta|^2$ is proportional to n_s. Assuming that n_s decays as $e^{-t/\tau}$, we then have that

$$\tau=\tfrac{1}{2}(\mathrm{Im}\omega')^{-1}\ . \tag{4.9}$$

Setting $D^{-1}(2k_F,\omega')$ equal to zero yields a quadratic equation in ω' having the two complex roots

$$\omega'=-i\pi\lambda\beta_c\hbar\,(\tfrac{1}{16}\omega_{2k_F}^2)\{1\pm[1-(16/\pi\hbar\beta_c\omega_{2k_F})^2\epsilon/\lambda]^{1/2}\}\ , \tag{4.10}$$

where $\ln(T/T_c)\sim(T-T_c)/T_c\equiv\epsilon$ and we have assumed $1\gg\frac{1}{16}[\lambda 7\zeta(3)(\omega_{2k_F}\beta_c/\pi)^2]$. Defining ϵ_0 as that value of ϵ at which the square-root term in (4.10) goes to zero,

$$\epsilon_0=\lambda(\tfrac{1}{16}\pi\beta_c\omega_{2k_F}\hbar)^2\ , \tag{4.11}$$

we find that, as a function of temperature, the frequencies of the $2k_F$ elementary excitations are

$$\omega'\simeq\pm(\lambda\epsilon)^{1/2}\omega_{2k_F}-\tfrac{1}{16}i\pi\lambda\beta_c\hbar\omega_{2k_F}^2\quad\text{for }\epsilon\gg\epsilon_0 \tag{4.12}$$

and

$$\omega'\simeq-i8\epsilon/\pi\beta_c\hbar$$

or

$$\omega'\simeq\tfrac{1}{8}[-i\pi\lambda\hbar\beta_c\omega_{2k_F}^2]+i8\epsilon/\pi\beta_c\hbar\quad\text{for }\epsilon\ll\epsilon_0\ . \tag{4.13}$$

For $\hbar\beta_c\omega_{2k_F}\sim1$ and $\lambda\sim\frac{1}{3}$, ϵ_0 is of the order of 0.01. Then the relaxation time τ is found to be

$$\tau\sim\hbar\pi\beta_c/16\epsilon\ ,\quad\text{for }\epsilon\ll\epsilon_0 \tag{4.14}$$

where we have used the smaller value of (4.13), and

$$\tau\sim8/\pi\lambda\beta_c\omega_{2k_F}^2\hbar\quad\text{for }\epsilon\geq\epsilon_0\ . \tag{4.15}$$

Equation (4.14) is identical to the relaxation time obtained from the time-dependent Ginzburg-Landau equation for pairing superconductors. For our model, however, τ is seen to level off at a constant for large ϵ instead of continuing to decrease as $1/\epsilon$. In this limit (4.12), τ is independent of the real part of ω' and thus of v_s.

For pairing superconductors the Ginzburg-Landau free energy F is involved in the time-dependent Ginzburg-Landau equation[18]

$$\hbar\gamma\frac{\partial\psi}{\partial t}=-\frac{\partial F}{\partial\psi^*}\ , \tag{4.16}$$

where γ is a new parameter, and ψ is related to Δ by $\psi=c^{1/2}\Delta$, with c given by Eq. (3.5). Equation (4.16) and the values of the parameters it contains can be obtained from the equation for the t matrix, a quantity describing the repeated scattering of a pair of electrons into other pair states. Since the $2k_F$-phonon propagator may be viewed as describing the repeated scattering of an electron-hole pair

which has singular behavior at $T = T_c$, we expect the Fourier transform of Eq. (4.8) to be similar to (4.16). In fact, we find that the thermodynamic energy obtained from (4.8) differs from the Ginzburg-Landau free energy by a Legendre transformation with respect to v_s.

The term proportional to ω in (4.8) corresponds to the left-hand side of (4.16) while the remaining terms are used to obtain the free energy. Multiplying by the proportionality factor $N(0)|\Delta|^2$, we get

$$\begin{aligned} G &\equiv N(0)\ln(T/T_c)|\Delta|^2 - \omega^2 N(0)|\Delta|^2/\lambda\omega_{2k_F}^2 \\ &\quad + 7\zeta(3)(\hbar\omega\beta_c/\pi)^2 N(0)|\Delta|^2/16 \\ &= [a - \omega^2 N(0)/\lambda\omega_{2k_F}^2 + 7\zeta(3) \\ &\quad \times (\hbar\omega\beta_c/\pi)^2 N(0)/16]|\Delta|^2 , \end{aligned} \tag{4.17}$$

where a is given by (2.11). Using $\omega = 2k_F v_s$, $N(0) = n/\pi E_F$, and Eqs. (1.7) and (3.5) we identify the $(\omega\beta_c)^2$ term with the kinetic energy contribution of the superfluid electrons to the free energy as discussed in Sec. III:

$$\begin{aligned} 7\zeta(3)(\hbar\omega\beta_c/\pi)^2 N(0)|\Delta|^2/16 &= cnm^* v_s^2|\Delta|^2/2 \\ &= \tfrac{1}{2}P_e v_s . \end{aligned} \tag{4.18}$$

Similarly the $(\omega/\omega_{2k_F})^2$ term represents the lattice kinetic energy. We define an effective mass m_1 by the relation

$$\begin{aligned} cnm_1 v_s^2|\Delta|^2/2 &\equiv \omega^2 N(0)|\Delta|^2/\lambda\omega_{2k_F}^2 \\ &= 2nm^* v_s^2|\Delta|^2/\lambda\omega_{2k_F}^2 . \end{aligned} \tag{4.19}$$

Thus, from (4.19) and (3.5) we find

$$m_1/m^* = 16\pi^2/\lambda(\hbar\omega_{2k_F}\beta_c)^2 7\zeta(3). \tag{4.20}$$

We get $m_1/m^* \sim 56$ if $\hbar\omega_{2k_F}\beta_c \sim 1$ and $\lambda \sim \frac{1}{3}$, but these values are uncertain. Introducing the lattice momentum $P_L = cnm_1 v_s|\Delta|^2$, (4.17) becomes

$$G = a|\Delta|^2 + \tfrac{1}{2}(P_e - P_L)v_s . \tag{4.21}$$

Since the Ginzburg-Landau free energy F involves the sum of the lattice and superelectron kinetic energies, the energy of Eq. (4.21) differs from F by a term $P_L v_s$. The resultant form of F is

$$F = a|\Delta|^2 + \tfrac{1}{2}(P_e + P_L)v_s = a|\Delta|^2(1 + \xi^{*2}q^2) , \tag{4.22}$$

where

$$\xi^* \equiv \xi(1 + m_1/m^*)^{1/2} \tag{4.23}$$

with ξ given by (3.9). We point out that (4.22) has the same form as the Ginzburg-Landau free energy for pairing superconductors, with the coherence distance ξ replaced with ξ^*. However, now the term $(\xi^* q)^2$ comes from the time dependence rather than the space dependence of the order parameter.

V. ESTIMATE OF THE PARACONDUCTIVITY

In this section we shall make an estimate of the paraconductivity and of the validity of mean-field theory, upon which our estimate is based. We employ standard techniques of mean-field theory,[19] in which the excess conductivity due to fluctuations, $\sigma' = \sigma - \sigma_N$, is given by summing the contributions from independent fluctuations of frequency ω. We shall use the variable q [see Eq. (1.4)] to designate the fluctuations. Allowed q values for periodic boundary conditions are integral multiples of $2\pi/L$, and q is related to ω by $q = m^*\omega/2\hbar k_F$. Then we have

$$\sigma' = \sum_q n_{sq} e^2 \tau/m^* , \tag{5.1}$$

where $n_{sq} = c|\Delta_q|^2 n$ is the density of superfluid electrons with $v_s = \hbar q/m^*$, and τ is their lifetime. The lifetime τ has been calculated in Eq. (4.15) for the temperature range of interest.

We point out that (5.1) depends in part for its validity upon all momentum change accruing to the electrons. In a fluctuation, P_e and P_L decay as $e^{-t/\tau}$. The decay of P_L has the effect of releasing $2k_F$ phonons, which will accelerate the electrons as an electric field will, scattering the electrons from the left to the right of the Fermi surface. In an electric field E, the total crystal momentum change due to the field, $\delta P = \delta P_e + \delta P_L$, is given by

$$\left(\frac{\delta P}{\delta t}\right)_f = \sum_q n_{sq} eE , \tag{5.2}$$

of which a certain fraction $m^*/(m_1 + m^*)$ of the increase in momentum due to the field goes to the electrons and the remainder to the lattice:

$$\left(\frac{\delta P_L}{\delta t}\right)_f = \frac{m_1}{m^* + m_1}\sum_q n_{sq} eE . \tag{5.3}$$

Now we neglect umklapp processes not related to τ and require that the lattice momentum (5.3) be released to the electrons at a time much shorter than τ. Then the total momentum change of the electrons due to the field becomes

$$\left(\frac{\delta P_e}{\delta t}\right)_f = \frac{m^*}{m^* + m_1}\sum_q n_{sq} eE + \frac{m_1}{m^* + m_1}\sum_q n_{sq} eE = \sum_q n_{sq} eE. \tag{5.4}$$

In other words, all of the increase in crystal momentum ends up in the electrons. The current is then given by

$$J = \left(\frac{\delta P_e}{\delta t}\right)_f e\tau/m^* = \sum_q n_{sq} e^2 E\tau/m^* , \tag{5.5}$$

which gives (5.1) as desired.

To calculate n_{sq}, we perform the necessary thermodynamic averaging of $|\Delta_q|^2$. We take our thermodynamic energy from (4.22) and neglect $|\Delta|^4$ terms:

$$F_q = a(1+\xi^{*2}q^2)|\Delta_q|^2 , \tag{5.6}$$

where ξ^* includes the effects of the lattice momentum. Thus

$$\langle |\Delta_q|^2 \rangle = \frac{\int d\Delta_q |\Delta_q|^2 e^{-F_q/k_BT}}{\int d\Delta_q e^{-F_q/k_BT}} = \frac{k_BT}{a(1+\xi^{*2}q^2)} ; \tag{5.7}$$

so

$$n_{sq} = cnk_BT/a(1+\xi^{*2}q^2) . \tag{5.8}$$

We may now write (5.1) as

$$\sigma' = \sum_q 8e^2(k_BT_c)^2 cn/m^{*}\pi^2\omega_{2k_F}^2 a_0\epsilon\hbar(1+\xi^{*2}q^2)\lambda . \tag{5.9}$$

Now let $\sum_q \to (L/2\pi)\int_{-\infty}^{\infty} dq$, where L is the chain length, and assume $\hbar\omega_{2k_F} \sim k_BT_c$ to get

$$\sigma' = 8e^2\xi_0/\epsilon^{1/2}(1+m_1/m^*)^{1/2}\pi\hbar S , \tag{5.10}$$

where we have used (3.9), (3.10), and (4.23). Here S is the cross-sectional area of a one-dimensional chain, or equivalently $1/S$ is the number of chains per unit area in the plane perpendicular to the chains.

One should note that in this model for $\epsilon > \epsilon_0$ the temperature dependence of (5.10) is $\epsilon^{-1/2}$ rather than $\epsilon^{-3/2}$ as in regular pairing theory. This difference arises, of course, from the fact that in this model τ is independent of ϵ in the range of temperatures in which we are interested [see (4.11) and (5.13)]. The usual $\epsilon^{-3/2}$ dependence of σ' is recovered only for values of $\epsilon \ll \epsilon_0 \simeq 0.01$.

We shall now substitute numbers relevant to TTF-TCNQ into (5.10). Using $E_F \simeq 0.2$ eV, $T_c \simeq 58$ °K, and $d = 3.8$ Å, we obtain $m^* \simeq 4.2m$ and $\xi_0 \simeq 70$ Å. From the data of Phillips *et al.*[14] we have $S \simeq 114$ Å^2. Using the estimates of (4.20) we have $(1+m_1/m^*)^{1/2} \simeq 7.5$. Thus we get

$$\sigma' \simeq (5\times 10^3)[T_c/(T-T_c)]^{1/2} \text{ mho/cm} . \tag{5.11}$$

If we assume a normal room-temperature conductivity for TTF-TCNQ of 2×10^3 mho/cm $= \sigma_{RT}$, then Eq. (5.11) predicts a paraconductivity at 68 °K of

$$\sigma'(T = 68\ ^\circ\text{K})/\sigma_{RT} \simeq 6 . \tag{5.12}$$

It is somewhat difficult to compare (5.12) to experiment[1] since we do not know the normal conductivity σ_N at $T \simeq 68$ °K. If we assume for instance $\sigma_N(T = 68\ ^\circ\text{K}) \simeq 4\sigma_{RT}$, then we have $\sigma/\sigma_{RT} \simeq 10$, in good agreement with the majority of measured TTF-TCNQ samples, but about an order of magnitude lower than the extraordinary conductivity peaks reported in a few samples. Further, at somewhat lower temperatures ($T \sim 60$ °K) Coleman *et al.* report values of $\sigma/\sigma_{RT} \sim 500$, which require a mean free path l of at least 2000 Å. In our model $v_F \simeq 10^7$ cm/sec and $\tau \simeq 3\times 10^{-13}$ sec (assuming $\hbar\omega_{2k_F} \sim k_BT_c$) for $\epsilon > \epsilon_0$, giving $l \simeq 300$ Å at best, a value far too low to explain such extraordinary conductivity values.

Now we examine the validity of mean-field theory for our model. We require that the fluctuation-induced superelectron density at some temperature $\epsilon > 0$ be less than the equilibrium superelectron density at $-\epsilon < 0$:

$$\sum_q n_{sq}/n < ca/b = c|\Delta|^2 = n_s/n . \tag{5.13}$$

The coefficient b is given by Eq. (2.12). We let $a = a_0\epsilon$ as before and define ϵ_{min} as that value which produces an equality in (5.13). Substituting (5.8) into (5.13) and performing the sum over q we get

$$(\epsilon_{min})^{3/2} = bT_cL/2a_0^2\xi_0(1+m_1/m^*)^{1/2} . \tag{5.14}$$

Using the same TTF-TCNQ values as before, we obtain from (5.14)

$$\epsilon_{min} \simeq 0.13 \to (T-T_c)_{min} \simeq 7.5\ ^\circ\text{K} . \tag{5.15}$$

We note that at ϵ_{min}, $n_s/n \simeq \frac{1}{4}$. We see that mean-field theory breaks down quickly as we approach T_c.

VI. CONCLUSION

We conclude that superconducting fluctuations above T_c leading to paraconductivity should be observed within a Fröhlich-type model. However, at least within mean-field theory, the Fröhlich model is incapable of accounting for the magnitude of the extraordinary conductivity peaks reported for some samples of TTF-TCNQ. Furthermore, the temperature dependence of the paraconductivity, which varies from $\epsilon^{-1/2}$ to $\epsilon^{-3/2}$ in the Fröhlich model, does not agree with the $\epsilon^{-3/2}$ dependence reported. We also conclude that the Fröhlich model is a viable theory for realizing superconductivity below T_c only if some attractive three-dimensional interchain interaction exists to lock the individual chains together so that the system has sufficient momentum to make the superconductivity long lived.

An accurate microscopic formulation of the Fröhlich model is needed to decide whether it can in any form give high paraconductivity values. The Fröhlich paraconductivity may involve diagrams which are not analogous to any of the usual BCS paraconductivity diagrams. It would be of interest to seek out other fluctuation phenomena which may be different in the Fröhlich and BCS theories. Perhaps most important, the experimental results should be verified by other methods of measuring the conductivity, such as two-probe methods and ac techniques.

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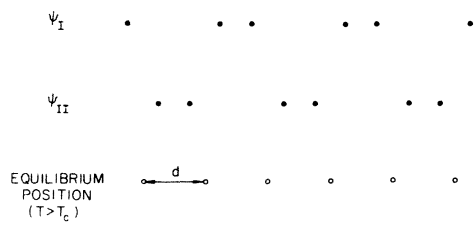

FIG. 3. ψ_I and ψ_{II} illustrate the two possible static Peierls distortions for a half-filled band.

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APPENDIX A: HALF-FILLED TIGHT-BINDING BAND

There are special problems involved in constructing running waves with a tight-binding band which is half-filled with electrons, such as may be the case for TTF-TCNQ with one extra electron per molecule in the chain. The gaps at $\pm k_F$ are then produced by a distortion of period $2d$ where d is the spacing between molecules along the chain. This could occur by displacing alternate atoms by $\pm \frac{1}{2}\delta d$. Displacements of opposite sign are shown as ψ_I and ψ_{II} in Fig. 3. Oscillations of molecules will give an alternation between ψ_I and ψ_{II} and no charge transport. Below T_c, ψ_I and ψ_{II} could represent the two stable positions of equal energy for the Peierls instability.

To construct running waves, one would have to build a wave packet by combining waves of the form $\exp[2ik_F(x - v_s t)]$ with a small spread of wave vectors centered about $2k_F$. For a half-filled band $2k_F = \pi/d$ and $\omega = \pi v_s/d$ so that the displacement at $x = nd$ would be proportional to $\cos(n\pi - \omega t) = (-1)^n \times \cos\omega t$, corresponding to a standing wave. The wave packet would include wave vectors differing slightly from $2k_F$ and the accompanying distortion would move with velocity v_s. The current density $n_s e v_s$ would be a maximum at the center of the wave packet. Above T_c, there would be fluctuations in charge density as well as in current. The wave packet and accompanying distortion would then move with velocity v_s, and in the center of the wave packet there would be a current flow $n_s e v_s$ where n_s is related to the magnitude of the distortion or the energy gap.

Below T_c, there is a free-energy minimum for each displacement ψ_I or ψ_{II} and a maximum for $\delta d = 0$. Thus the system would have to surmount an energy barrier in going from ψ_I to ψ_{II} and could be locked in one of the two positions. This would give a true semiconducting or insulating phase. However, there could be paraconductivity above T_c where the energy barriers are vanishing or at least very small. Thus the absence of superconducting behavior below T_c is not surprising.

APPENDIX B

In this appendix we illustrate the techniques used to evaluate integrals in the tight-binding approximation by calculating the coefficients a and b of Eq. (2.10).

The Taylor-series expansion in $|\Delta|^2$ of (2.9) gives

$$a = -\sum_k \tanh[\tfrac{1}{2}\beta\epsilon(k)]\,\frac{1}{2\epsilon(k)} + \frac{N(0)}{\lambda} \tag{B1}$$

and

$$b = \sum_k \frac{1}{4\epsilon^2}[(1/\epsilon)\tanh\tfrac{1}{2}\beta\epsilon - (\tfrac{1}{2}\beta)\,\mathrm{sech}^2\tfrac{1}{2}\beta\epsilon]\ . \tag{B2}$$

The replacement $\sum_k \to \int_{-E_F}^{E_F} N(\epsilon)\,d\epsilon$ with

$$N(\epsilon) = N(0)/(1 - \epsilon^2/E_F^2)^{1/2} \tag{B3}$$

results in the following equations for a and b:

$$a = -N(0)\int_0^{E_F} d\epsilon \tanh(\tfrac{1}{2}\beta\epsilon)\epsilon^{-1}(1 - \epsilon^2/E_F^2)^{-1/2} + N(0)/\lambda\ , \tag{B4}$$

$$b = [\tfrac{1}{2}N(0)]\int_0^{E_F} d\epsilon\,[\epsilon^{-1}\tanh(\tfrac{1}{2}\beta\epsilon) - \tfrac{1}{2}\beta\,\mathrm{sech}^2(\tfrac{1}{2}\beta\epsilon)] \times \epsilon^{-2}(1 - \epsilon^2/E_F^2)^{-1/2}\ . \tag{B5}$$

We evaluate a by introducing a cutoff X such that $2/\beta \ll X \ll E_F$. Thus for $\epsilon < X$, $(1 - \epsilon^2/E_F^2)^{1/2} \sim 1$ and for $\epsilon > X$, $\tanh\tfrac{1}{2}\beta\epsilon \sim 1$. Then using the equation that gives T_c,

$$\frac{1}{\lambda} \simeq \int_0^{E_F} \frac{d\epsilon}{\epsilon(1 - \epsilon^2/E_F^2)^{1/2}} \tanh\left(\frac{\epsilon}{2k_B T_c}\right)\ , \tag{B6}$$

we obtain

$$a = -N(0)\ln(T_c/T)\ . \tag{B7}$$

Similar analysis of b yields a value essentially identical to the coefficient of the term proportional to $|\Delta|^4$ for a BCS superconductor:

$$b \simeq 0.106\,N(0)/(k_B T_c)^2\ . \tag{B8}$$

Note added in proof. More recent results by Patton and Sham for a non-half-filled band and by Strässler and Toombs (preprint) indicate a nonzero result for the paraconductivity associated with these diagrams.

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