

strong support of such suggestions.

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### POSSIBILITY OF ONE-DIMENSIONAL SUPERCONDUCTIVITY\*

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Recently attention has been drawn toward the possibility that long organic molecules might exhibit superconductivity.<sup>1</sup> At the same time the question has, however, been raised<sup>2</sup> of whether or not there might be special effects associated with the case of one-dimensional motion which might make the occurrence of superconductivity in one dimension quite different from its occurrence in three dimensions. Indeed, there is a well-known theorem based on thermodynamic considerations that no phase exhibiting long-range order can exist in one dimension.<sup>3</sup> It has been suggested that this theorem is sufficiently general to cover superconductive ordering.<sup>4</sup> The theorem is predicated on the assumption of short-range forces and it may be argued that the Hamiltonian which forms the basis of the BCS<sup>5</sup> theory of superconductivity essentially involves an infinite-range force. But the actual physical system which the BCS Hamiltonian is intended to describe does, of course, only contain forces of limited range, and there are important modifications of the BCS theory which are required to take into account the terms in the interaction Hamiltonian which are omitted from the reduced Hamiltonian of BCS. These terms, as noted by Bogoliubov, Tolmachev, and Shirkov,<sup>6</sup> Anderson,<sup>7</sup> Rickayzen,<sup>8</sup> and Prange<sup>9</sup> make it possible for the system to exhibit compressional modes of vibration and to satisfy the requirements of gauge invariance. The purpose of this note is to point out

that the compressional modes play a much more dominant role in one dimension than they do in three dimensions, and prevent the establishment of the long-range order which is required for superconductive phenomena.

Let the required compressional modes of vibration of particles which are constrained to move in only one direction, say along the  $x$  axis, be described by the creation and annihilation operators  $a_k^\dagger$  and  $a_k$  where  $k$  is the wave number of the running wave. (Throughout this paper we choose units in which Planck's constant equals  $2\pi$ .) In terms of these quantized operators, the particle density operator at the position  $x$  has the following standard expansion:

$$\rho(x) = \sum_k \frac{ink}{(2m n \omega_k L)^{1/2}} (a_k^\dagger - a_{-k}) e^{-ikx}, \quad (1)$$

where  $m$  is the mass of the individual fermions,  $n$  the linear particle density,  $L$  the length of quantization, and  $\omega_k$  the frequency of  $k$ th mode. The equation of continuity requires that there be a velocity field present which is given by the following simple equation:

$$m^{-1}q(x) = v\rho(x)/n. \quad (2)$$

$v = \omega_k/k$  is the velocity of propagation of the compressional waves in the long-wavelength limit.  $q(x)$  can be interpreted as the local value of the mean pairing momentum of the fermions in the

superfluid, and is proportional to the gradient of the phase of the superfluid. Consequently, we can determine the phase of the superfluid at any point  $x$  by simply integrating over the local values of the mean pairing momentum:

$$\begin{aligned}\varphi(x) &= 2 \int^x q(x) dx \\ &= -2mv \sum_k (2mn\omega_k L)^{-1/2} (a_k^\dagger + a_{-k}) e^{-ikx}. \quad (3)\end{aligned}$$

As discussed by Yang,<sup>10</sup> the characteristic superconducting properties of a metal in its superconductive state are a result of a nonzero value of a certain Green's function  $G(x, x')$  for large values of the difference  $x-x'$ . This Green's function is defined by the equation

$$\begin{aligned}G(x, x') &= \langle \psi_\uparrow(x) \psi_\downarrow(x) \psi_\downarrow^\dagger(x') \psi_\uparrow^\dagger(x') \rangle, \\ &= \langle N | \psi_\uparrow(x) \psi_\downarrow(x) | N+2 \rangle \\ &\quad \times \langle N+2 | \psi_\downarrow^\dagger(x) \psi_\uparrow^\dagger(x) | N \rangle + \dots, \\ &= F(x) F^*(x) + \dots; \quad (4)\end{aligned}$$

where the arrows indicate electron spin orientation and the terms not exhibited in the closure expansion do not contribute to the "off-diagonal long-range order." The matrix elements are taken between the states of  $N$  and  $N+2$  fermions and the notation of Gor'kov<sup>11</sup> for the matrix element of the pair annihilation operator has been introduced. In order for the first term in Eq. (4) to give long-range order, it is necessary that the Fourier transform of the Gor'kov function should possess a delta-function spike. As there is no preferred value of mean pairing momentum in the present problem, this spike will necessarily have to be located at the origin in reciprocal space. Writing the Gor'kov function in terms of its modulus and phase,

$$F(x) = \Delta \langle e^{i\varphi(x)} \rangle, \quad (5)$$

we obtain the strength of the delta function from the integral

$$F_0 = \frac{1}{L} \int F(x) dx = \Delta e^{-M}, \quad (6)$$

where the exponential factor is defined by the expression

$$e^{-M} \equiv \langle e^{i\varphi(x)} \rangle. \quad (7)$$

The average is to be taken over the equilibrium ensemble of states. Because of the translational invariance, the spatial integration is redundant

and can be dropped.

The point of this paper is that the value of  $M$  in Eq. (7) is infinitely large for one-dimensional geometry and consequently that the strength of the long-range order is vanishingly small. This is most readily seen by noting that the present problem is mathematically identical to the familiar problem posed by the question of long-range order in a one-dimensional vibrating lattice. Using the same expression for the quantized density operator as in Eq. (1), it is possible here, in dealing with a discrete lattice, to introduce the displacement  $\xi(x)$  of a lattice point from its unperturbed position  $x$ . The divergence of this displacement operator is proportional to the density, and consequently the displacement operator has the following expansion:

$$\xi(x) = \sum_k (2mn\omega_k L)^{-1/2} (a_k^\dagger + a_{-k}) e^{-ikx}. \quad (8)$$

Now suppose that the undisplaced lattice points have a spacing corresponding to the reciprocal lattice vector  $G$ . Then the square root of the Debye-Waller factor<sup>12</sup> for the vibrating lattice is given by the expression

$$e^{-M} = \frac{1}{L} \int \langle e^{-iG\xi(x)} \rangle dx. \quad (9)$$

If in this problem we substitute for the value of the reciprocal lattice vector

$$G = 2mv, \quad (10)$$

then we see that in Eq. (7) we are dealing simply with the Debye-Waller factor of a one-dimensional lattice. It is well known that the Debye-Waller factor vanishes for this case, as there is no long-range lattice order for one-dimensional geometry. For the sake of completeness, we merely remind the reader that this can be seen from the expansion of the exponential functions in Eq. (9). Identification of the first nontrivial terms on the two sides of the equation gives

$$M = \frac{G^2}{2mnL} \sum_k \omega_k^{-1} (\langle N_k \rangle + \frac{1}{2}) = \frac{G^2}{4\pi m v} \int \frac{dk}{k}, \quad (11)$$

where in passing to the integral we restrict the integration to only positive values of the wave number, and have taken the quantum mechanical expectation value over the ground state of the system. Then all of the occupation numbers for the oscillators vanish and only the zero-point motion contributes to the smearing out of the lattice in reciprocal space. Because of the log-

arithmetic divergence in the long-wavelength limit,<sup>13</sup> this smearing is complete and no vestige of long-range order remains.<sup>14</sup>

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<sup>10</sup>C. N. Yang, Rev. Mod. Phys. **34**, 694 (1962).

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Gor'kov's limiting approach to the equal-time case is superfluous, because of the anticommuting of the annihilation operators.

<sup>12</sup>For a general discussion of the theory of the Debye-Waller factor, see M. Born, Rept. Progr. Phys. **9**, 294 (1942).

<sup>13</sup>The upper limit of integration should be taken as  $\Delta$  divided by the Fermi velocity, as our equations are valid only for wavelengths longer than the coherence length.

<sup>14</sup>For the three-dimensional case there is no divergence, because of the additional factor of  $k^2$  in the integrand, and we find  $M \approx (\Delta/\epsilon_F)^2$ , where  $\epsilon_F$  is the Fermi energy. For a typical superconductor this is of the order of  $10^{-8}$ , corresponding to a completely negligible weakening of the long-range order. It is interesting further to note that if the collective oscillations do not satisfy the linear dispersion relation of sound waves, then an additional factor of  $\omega_k/k$  appears in the integrand of Eq. (11). Thus, for a cylindrical thread of plasma of radius  $a$  and of bulk plasma frequency  $\omega_p$  immersed in a medium of dielectric constant  $\epsilon$ , the dispersion relation is

$$\omega_k/k = a\omega_p [(-\frac{1}{2}\epsilon) \ln(ka)]^{1/2}$$

and the divergence is aggravated. Allowing for plasma oscillations in three dimensions increases the dependence of  $M$  upon  $\Delta/\epsilon_F$  to the first power, which, however, is still negligibly small. The effect of retardation on the one-dimensional plasma oscillations, which brings in the vector potential and could alter the phase considerations, is currently under investigation.

## HARMONIC GENERATION OF MICROWAVE PHONONS IN QUARTZ

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Bömmel and Dransfeld<sup>1</sup> and Jacobsen<sup>2</sup> have demonstrated that microwave phonons can be generated by the piezoelectric effect at the end surface of quartz placed in the electric field of a re-entrant cavity. The present paper shows that second and third harmonics of the fundamental microwave frequency are also generated. The experiment was originally undertaken to measure the higher order elastic constants which are important in the "collinear processes"<sup>3,4</sup> by which a longitudinal acoustic wave interacts with thermal phonons. The nonlinearity due to this interaction, however, was found to be much smaller than that present in the generation of the acoustic waves themselves. Second-harmonic generation in nonpiezoelectric  $Z$ -cut quartz has also been observed. It was much smaller than in piezo-

electric quartz and of the magnitude to have been caused by the electric stress. This result is contrary to some of Shiren's<sup>5</sup> qualitative measurements of harmonic generation in piezoelectric quartz, which were attributed to the electric stress, and shows that acoustic wave generation is not limited to the relatively rare piezoelectric materials.

Microwave phonons are generated at the end surface of a piezoelectric quartz rod placed in the high electric field region of a re-entrant 4.5-Gc/sec cavity shown in Fig. 1. This cavity is excited by a 0.5- $\mu$ sec pulse of electromagnetic energy which has passed through a low-pass filter to eliminate any harmonics above 4.5 Gc/sec which might have been present in the pulsed microwave source. The second-harmonic content