Individual metallic single-wall carbon nanotubes show unusual non-Ohmic transport behaviors at high bias fields. For low resistance contact samples, the differential conductance $dI/dV$ increases with increasing bias, reaching a maximum at $\sim 100$ mV. As the bias increases further, $dI/dV$ drops dramatically [Yao et al., Phys. Rev. Lett. 84, 2941, 2000]. The higher the bias, the system behaves in a more normal (Ohmic) manner. This so-called zero-bias anomaly is temperature-dependent (50–150 K). We propose a new interpretation. Supercurrent runs in the graphene wall below $\sim 150$ K. The normal conduction-electron currents run outside the wall, which are subject to the scattering by phonons and impurities. The currents along the tube induce circulating magnetic fields and eventually destroy the supercurrent in the wall at high enough bias, and restore the Ohmic behavior. If the prevalent ballistic electron model is adopted, then the scattering effects cannot be discussed.

I. INTRODUCTION

In 2000, Yao, Kane and Dekker [1] reported the high-field transports in metallic Single-Wall carbon Nanotubes (SWNT). In Fig. 1 we reproduced their $I$-$V$ curves, after Ref. [1], Fig. 1. At low fields (voltage $\sim 30$ mV), the currents show temperature-dependent dips near the origin, exhibiting non-Ohmic behaviors while at the high fields ($\sim 5$ V) the resistance $R$ versus the bias voltage $V$ shows a relation:

$$R = R_0 + V/I_0 \quad (\text{high } V),$$

where $R_0$ and $I_0$ are constants. The original authors discussed the low-field behavior in terms of one-dimensional (1D) Luttinger liquid (LL) model. Many experiments however indicate that the electrical transports in SWNT have a two-dimensional (2D) character. In fact, the conductivity in individual nanotubes depends on the circumference and the pitch characterizing a space-curve (2D). Hence the nanotube physics requires a 2D theory. In the present work, we present a unified microscopic theory of both low- and high-field conductivities. Carbon nanotubes are discovered by Iijima. The important questions are how the electrons or other charged particles traverse the nanotubes and whether these particles are scattered by impurities and phonons or not. To answer these questions, we need the electron energy band structures. Wigner and Seitz (WS) [4] developed the WS cell model to study the ground state of a metal. Starting with a given lattice, they obtain a Brillouin zone in the $k$-space and construct a Fermi surface. This method has been successful for cubic crystals including the face-centered cubic (fcc), the body-centered cubic (bcc), diamond and zinblende lattices. If we apply the WS cell model to graphene, we then obtain a gapless semiconductor, which is not experimentally observed [2]. We will overcome this difficulty by taking a different route in Sec. II.

SWNTs can be produced by rolling graphene sheets into circular cylinders of about one nanometer (nm) in diameter and microns ($\mu$m) in length. The electrical conduction in SWNTs depends on the circumference and pitch, and can be classified into two groups: either...
voltages of FIG. 2: Current-voltage curves of metallic SWNT at gate voltages of 88.2 mV (trace A), 104.1 mV (trace B) and 120.0 mV (trace C). After Tans et al. in Ref. [9], Fig. 2.

In our previous work [3], we have shown that this division in two groups arises as follows. A SWNT is likely to have an integral number of carbon hexagons around the circumference. If each pitch contains an integral number of hexagons, then the system is periodic along the tube axis, and “holes” (not “electrons”) can move along the tube. Such a system is semiconducting and its electrical conductivity increases with the temperature, and is characterized by an activation energy ε. The energy ε has a distribution since both pitch and circumference have distributions. The pitch angle is not controlled in the fabrication processes. There are far more numerous cases where the pitch contains an irrational number of hexagons. In these cases, the system shows a metallic behavior experimentally observed.

We primarily deal with the metallic SWNTs in the present work. Before dealing with high-field transports, we briefly discuss the low-field transports. Tans et al. [3] measured the electrical currents in metallic SWNTs under bias and gate voltages. Their data from Ref. [3], Fig. 2, are reproduced in Fig. 2. The currents versus the bias voltage are plotted in Fig. 2 at three gate voltages: A (88.2 mV), B (104.1 mV), C (120.0 mV). Significant features are:

(i) A non-Ohmic behavior is observed for all, that is, the currents are not proportional to the bias voltage except for high bias. The gate voltage charges the tube. The Coulomb (charging) energy of the system having charge Q is represented by

$$E_{\text{Coul}} = Q^2 / 2C,$$

where C is the total capacitance of the tube.

(ii) The current near the origin appears to be constant for different gate voltages V_{\text{gate}}. (A)–(C). This feature was confirmed by later experiments. [8, 10] The current does not change for small varying gate voltage in a metallic SWNT (while the current (magnitude) decreases in a semiconducting SWNT).

(iii) The current at gate voltage V_{\text{gate}} = 88.2 mV (A) reverts to the normal resistive behavior after passing the critical bias voltages on both (positive and negative) sides. Similar behaviors are observed for V_{\text{gate}} = 104.1 mV (B) and V_{\text{gate}} = 120.0 mV (C).

(iv) The flat current is destroyed for higher bias voltages (magnitudes). The critical bias voltage becomes smaller for higher gate voltages.

(v) There is a restricted V_{\text{gate}}-range (view window) in which the horizontal stretch can be observed. Tan et al. [9] interpreted the flat currents near V_{\text{bias}} = 0 in Fig. 2 in terms of a ballistic electron model [2]. We propose a differing interpretation of the data in Fig. 2 based on the Cooper pair [11] (pairon) carrier model. Pairons move as bosons, and hence they are produced with no activation energy factor. All features (i)–(v) can be explained simply with the assumption that the nanotube wall is in the superconducting state as explained below.

The supercurrent runs without obeying Ohm’s law. This explains the feature (i). The supercurrents can run with no resistance due to the phonon and impurity scattering and with no bias voltage. Bachtold et al. [12] observed by scanned probe microscopy that the currents run with no voltage change along the tube in metallic SWNTs. The system is in a superconducting ground state, whose energy $-E_g$ is negative relative to the ground-state energy of the Fermi liquid (electron) state. If the total energy E of the system is less than the condensation energy $E_g$,

$$E = K + E_{\text{Coul}} + E_\phi \leq E_g,$$  \hspace{1cm} (3)

where K is the kinetic energy of the conduction electrons and the pairons, and

$$E_\phi = QV_{\text{bias}}$$  \hspace{1cm} (4)

is the Coulomb field energy, then the system is stable. Experiments in Fig. 2 were done at 5 mK. Hence, we may drop the kinetic energy K hereafter. The superconducting state is maintained and the currents run unchanged if the bias voltage $V_{\text{bias}}$ is not too large so that the inequality (3) holds. This explains the horizontal stretch feature (ii).

If the bias voltage is high enough so that the inequality symbol in Eq. (3) is reversed, then normal currents revert and exhibit the Ohmic behavior, which explains the feature (iii).

The feature (iv) can be explained as follows. For higher $V_{\text{gate}}$ there are more amounts of charge, and hence the charges $Q_A$, $Q_B$, $Q_C$ for the three cases (A, B, C) satisfy the inequalities:

$$Q_A < Q_B < Q_C.$$  \hspace{1cm} (5)
The horizontal stretches are longer for smaller bias voltages. At the end of the stretch \( (V_{\text{bias,max}}) \) the system energy equals the condensation energy \( E_g \). Hence, we obtain from Eq. (3) after dropping the kinetic energy \( K \)

\[
E_{g,\max} = QV_{\text{bias,max}} \equiv QV_{\max} = E_g - E_{\text{Coul}} = E_g - Q^2/2C. \tag{6}
\]

Using Eq. (5), we then obtain

\[
V_{\max,A} > V_{\max,B} > V_{\max,C}, \tag{7}
\]

which explains the feature (iv).

The horizontal stretch becomes shorter as the gate voltage \( V_{\text{gate}} \) is raised; it vanishes when \( V_{\text{gate}} \) is a little over 120.0 mV. The limit is given by

\[
E_{g,\max} = E_g - E_{\text{Coul}} = E_g - Q^2/2C = 0. \tag{8}
\]

If the charging energy \( E_{\text{Coul}} \) exceeds the condensation energy \( E_g \), then there are no more supercurrents, which explains the feature (v). Clearly the important physical property in our pairon model is the condensation energy \( E_g \).

In the currently prevailing theory \[2\], it is argued that the electron (fermion) motion becomes ballistic at a certain quantum condition. But all fermions are known to be subject to scattering. It is difficult to justify the reason why the ballistic electron is not scattered by impurities and phonons, which naturally exist in nanotubes. Yao, Kane and Dekker \[1\] emphasized the importance of phonon scattering effects in their analysis of their data in Fig. 1. The Cooper pairs \[1\] in supercurrents, as is known, can run with no resistance (due to impurities and phonons). Clearly the experiments on the currents shown in Fig. 1 are temperature-dependent, indicating the importance of the electron-phonon scattering effect. If the ballistic electron model is adopted, then the phonon scattering cannot be discussed within the model’s framework. We must go beyond the ballistic electron model.

If the SWNT is unrolled, then we have a graphene sheet, which can be superconducting at a finite temperature. We first study the conduction behavior of graphene in Sec. III starting with the honeycomb lattice and introducing “electrons” and “holes” based on the orthogonal unit cell. Phonons are generated based on the same orthogonal unit cell. In Sec. III we treat phonons and phonon-exchange attraction. In Sec. 4, we construct a Hamiltonian suitable for the formation of the Cooper pairs. We derive, in Sec. 5, the linear dispersion relation for the center-of-mass motion of the pairons. The pairons moving with a linear dispersion relation undergoes a Bose-Einstein condensation (BEC) in 2D, which is shown in Sec. 6. Zero-bias anomaly is discussed in Sec. 7.

II. GRAPHENE

Following Ashcroft and Mermin \[13\], we adopt the semiclassical model of electron dynamics in solids. In the semiclassical (wave packet) theory, it is necessary to introduce a \( k \)-vector

\[
k = k_x \hat{e}_x + k_y \hat{e}_y + k_z \hat{e}_z, \tag{9}
\]

\( \hat{e}_x, \hat{e}_y \) and \( \hat{e}_z \) are Cartesian orthonormal vectors since the \( k \)-vectors are involved in the semiclassical equation of motion:

\[
h \dot{k} \equiv h \frac{dk}{dt} = q(E + \nu \times B), \tag{10}
\]

where \( E \) and \( B \) are the electric and magnetic fields, respectively, and the vector

\[
\nu = \frac{\partial \varepsilon}{\partial \mathbf{k}} \tag{11}
\]

is the electron velocity where \( \varepsilon \) is the energy. The 2D crystals such as graphene can also be treated similarly, only the \( z \)-components being dropped. The choice of the Cartesian axes and the unit cell is obvious for the cubic crystals. We must choose an orthogonal unit cell also for the honeycomb lattice, as shown below.

Graphene forms a 2D honeycomb lattice. The WS unit cell is a rhombus shown in Fig. 3(a). The potential energy \( V(\mathbf{r}) \) is lattice-periodic:

\[
V(\mathbf{r} + \mathbf{R}_{mn}) = V(\mathbf{r}), \tag{12}
\]

where

\[
\mathbf{R}_{mn} \equiv m \mathbf{a}_1 + n \mathbf{a}_2 \tag{13}
\]

are Bravais vectors with the primitive vectors \( \mathbf{a}_1, \mathbf{a}_2 \) and integers \((m, n)\). In the field theoretical formulation, the field point \( \mathbf{r} \) is given by

\[
\mathbf{r} = \mathbf{r}' + \mathbf{R}_{mn}, \tag{14}
\]

where \( \mathbf{r}' \) is the point defined within the standard unit cell. Equation (12) describes the 2D lattice periodicity but does not establish the \( k \)-space, which is explained below.
To see this clearly, we first consider an electron in a simple square (sq) lattice. The Schrödinger wave equation is

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 \psi(\mathbf{r}) + V_{sq}(\mathbf{r})\psi(\mathbf{r}).$$  \hspace{1cm} (15)

The Bravais vector for the sq lattice, $\mathbf{R}_{mn}^{(0)}$, is

$$\mathbf{R}_{mn}^{(0)} \equiv m\mathbf{a}_x + n\mathbf{a}_y = m\mathbf{a}_x + n\mathbf{a}_y, \quad (a = \text{lattice constant}).$$ \hspace{1cm} (16)

The system is lattice periodic:

$$V_{sq}\left(\mathbf{r} + \mathbf{R}_{mn}^{(0)}\right) = V_{sq}(\mathbf{r}).$$ \hspace{1cm} (17)

If we choose a set of Cartesian coordinates $(x,y)$ along the sq lattice, then the Laplacian term in Eq. (15) is given by

$$\nabla^2 \psi(x,y) = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) \psi(x,y).$$ \hspace{1cm} (18)

If we choose a periodic square boundary with the side length $Na, N = \text{integer}$, then there are 2D Fourier transforms and (2D) $k$-vectors.

We now go back to the original graphene system. If we choose the $x$-axis along either $\mathbf{a}_1$ or $\mathbf{a}_2$, then the potential energy field $V(\mathbf{r})$ is periodic in the $x$-direction, but it is aperiodic in the $y$-direction. For an infinite lattice the periodic boundary is the only acceptable boundary condition for the Fourier transformation. Then, there is no 2D $k$-space spanned by 2D $k$-vectors. If we omit the kinetic energy term, then we can still use Eq. (12) and obtain the ground state energy (except the zero point energy).

We now choose the orthogonal unit cell shown in Fig. 3(b). The unit has side lengths

$$b_1 = \sqrt{3}a_0, \quad b_2 = 3a_0,$$ \hspace{1cm} (19)

where $a_0$ is the nearest neighbor distance between two C’s. The unit cell has 4 C’s. The system is lattice-periodic in the $x$- and $y$-directions, and hence there are 2D $k$-space.

The “electron” (“hole”) is defined as a quasi-electron that has an energy higher (lower) than the Fermi energy $\varepsilon_F$ and “electrons” (“holes”) are excited on the positive (negative) side of the Fermi surface with the convention that the positive normal vector at the surface points in the energy-increasing direction.

The “electron” (wave packet) may move up or down along the $y$-axis to the neighboring hexagon sites passing over one C$^+$. The positively charged C$^+$ acts as a welcoming (favorable) potential valley for the negatively charged “electron”, while the same C$^+$ acts as a hindering potential hill for the positively charged “hole”. The “hole”, however, can move horizontally along the $x$-axis without meeting the hindering potential hills. Thus the easy channel directions for the “electrons” (“holes”) are along the $y$-($x$-)axes.

Let us consider the system (graphene) at 0 K. If we put an electron in the crystal, then the electron should occupy the center O of the Brillouin zone, where the lowest energy lies. Additional electrons occupy points neighboring the center O in consideration of Pauli’s exclusion principle. The electron distribution is lattice-periodic over the entire crystal in accordance with the Bloch theorem.

Carbon (C) is a quadrivalent metal. The first few low-lying energy bands are completely filled. The uppermost partially filled bands are important for the transport properties discussion. We consider such a band. The Fermi surface, which defines the boundary between the filled and unfilled $k$-spaces (area) is not a circle since the $x$-$y$ symmetry is broken. The “electron” effective mass is lighter in the $y$-direction than perpendicular to it. Hence the electron motion is intrinsically anisotropic. The negatively charged “electron” is near the positive ions C$^+$ and the “hole” is farther away from C$^+$. Hence, the gain in the Coulomb interaction is greater for the “electron”. That is, the “electron” is more easily activated. Thus, the “electrons” are the majority carriers at zero gate voltage.

We may represent the activation energy difference by

$$\varepsilon_1 < \varepsilon_2.$$ \hspace{1cm} (20)

The thermally-activated (or excited) electron densities are given by

$$n_j(T) = n_j e^{-\varepsilon_j/\hbar T},$$ \hspace{1cm} (21)

where $j = 1$ and 2 denote the “electron” and “hole”, respectively. The prefactor $n_j$ is the density at the high-temperature limit.

**III. PHONONS AND PHONON EXCHANGE ATTRACTION**

Phonons are bosons corresponding to the running normal modes of the lattice vibrations. They are characterized by the energy $\hbar\omega$, where $\omega$ is the angular frequency, and the momentum vector $h\mathbf{q}$, whose magnitude is $2\pi\hbar$ times the wave numbers. The $q$-vector for phonons is similar to the $k$-vector for the conduction electrons. The phonon with $\mathbf{q}$ represents a plane-wave proceeding in the $\mathbf{q}$-direction. The frequency $\omega$ is connected with the $q$-vector through the dispersion relation

$$\omega = \omega(\mathbf{q}).$$ \hspace{1cm} (22)

The excitation of the phonons can be discussed based on the same rectangular unit cell introduced for the conduction electrons. We note that phonons can be discussed naturally based on the orthogonal unit cells. [It is difficult to describe phonons in the WS cell model.] For example, longitudinal (transverse) phonons proceeding upwards are generated by imagining a set of plates
each containing a number of rectangular cells executing small oscillations vertically (horizontally). A longitudinal wave proceeding in the crystal axis $x$, is represented by

$$u_q \exp(-i\omega_q t + i\mathbf{q} \cdot \mathbf{r}) = u_q \exp(-i\omega_q t + i\mathbf{x}),$$

where $u_q$ is the displacement in the $x$-direction. If we imagine a set of parallel plates containing a great number of ions fixed in each plate, then we have a realistic picture of the lattice vibration mode. The density of ions changes in the $x$-direction. Hence, the longitudinal modes are also called the density-wave modes. The transverse wave mode can also be pictured by imagining a set of parallel plates containing a great number of ions fixed in each plate executing the transverse displacements. Notice that this mode generates no charge-density variation.

The Fermi velocity $v_F$ in a typical metal is of the order $10^6$ m/s while the speed of sound is of the order $10^2$ m/s. The electrons are likely to move quickly to negate any electric field generated by the density variations associated with the lattice wave. In other words, the electrons may follow the lattice waves instantly. Given a traveling normal wave mode in Eq. (21), we may assume electrons may follow the lattice waves instantly. Given a traveling normal wave mode in Eq. (21), we may assume electrons follow phonons immediately for all $\omega_q$, the coefficient $C_q$ can be regarded as independent of $\omega_q$. If we further assume that the deviation is linear in the scalar product $u_q \cdot \mathbf{q} = q u_q$ and again in the electron density $n(r)$, we then obtain

$$C_q = A_q u_q n(r).$$

This is called the deformation potential approximation. The dynamic response factor $A_q$ is necessarily complex since the traveling wave is represented by the exponential form. Complex conjugation of Eq. (24) yields $C_q^* \exp(i\omega_q t - i\mathbf{q} \cdot \mathbf{r})$. Using this form we can reformulate the electron’s response, but the physics must be the same. From this consideration, we obtain

$$A_q = A_q^*.$$  

Each normal mode corresponds to a harmonic oscillator characterized by $(\mathbf{q}, \omega_q)$. The displacements $u_q$ can be expressed as

$$u_q = \left(\frac{\hbar}{2\omega_q}\right)^{1/2} (a_q - a_q^\dagger),$$

where $(a_q, a_q^\dagger)$ are operators satisfying the Bose commutation rules:

$$[a_q, a_p^\dagger] = a_q a_p^\dagger - a_p^\dagger a_q = \delta_{pq},$$

$$[a_q, a_p] = [a_q^\dagger, a_p^\dagger] = 0.$$  

Let us now construct an interaction Hamiltonian $H_F$, which has the dimensions of an energy and which is Hermitian. Using Eqs. (22) and (23), we obtain

$$H_F = \int d^3r \frac{1}{2} \sum_q [A_q u_q \exp(i\mathbf{q} \cdot \mathbf{r}) n(r) + h.c.],$$

where $h.c.$ denotes the Hermitian conjugate. This Hamiltonian $H_F$ can be expressed as

$$H_F = \sum_k \sum_q \frac{1}{2} \left( V_q c_{k+q}^\dagger c_{kq} + h.c. \right),$$

$$V_q \equiv A_q (\hbar/2\omega_q)^{1/2} i q,$$

where $c, c^\dagger$ are electron operators satisfying the Fermi anticommutation rules:

$$\{ c_k, c_{k'}^\dagger \} = c_k c_{k'}^\dagger + c_{k'}^\dagger c_k = \delta_{k,k'},$$

$$\{ c_k, c_{k'} \} = \{ c_k^\dagger, c_{k'}^\dagger \} = 0.$$  

The $H_F$ in Eq. (30) is the Fröhlich Hamiltonian. In the process of deriving Eq. (30), we found that the $H_F$ is applicable for the longitudinal phonons only. As noted earlier, the transverse lattice normal modes generate no charge density variations, making its contribution to $H_F$ negligible.

IV. THE FULL HAMILTONIAN

Bardeen, Cooper and Schrieffer (BCS) published a historic theory of superconductivity in 1957. Following BCS, Fujita and his collaborators developed a quantum statistical theory of superconductivity in a series of papers. Following this theory, we construct a generalized BCS Hamiltonian in this section.

In the ground state there are no currents for any system. To describe a supercurrent, we must introduce moving pairons, that is, pairons with finite center-of-mass (CM) momenta. Creation operators for “electron” (1) and “hole” (2) pairons are defined by

$$B_{12}^{(1)\dagger} = B_{k1^k k2^k}^{(1)\dagger} \equiv c_{1^k}^\dagger c_{2^k}, \quad B_{34}^{(2)\dagger} = c_{3^4}^{(2)\dagger} c_{3^4}.$$  

We calculate the commutators among $B$ and $B^\dagger$, and obtain

$$[B_{12}^{(1)}, B_{34}^{(j)}] = 0, \quad [B_{12}^{(1)}, B_{12}^{(j)}]^2 = 0,$$

where

$$[B_{12}^{(j)}, B_{34}^{(j)}] = \begin{cases} 1 - n_{1^k}^{(j)} - n_{2^k}^{(j)} & \text{if } k_1 = k_3 \text{ and } k_2 = k_4 \\ c_{1^k}^{(j)} c_{4^k}^{(j)dagger} & \text{if } k_1 = k_3 \text{ and } k_2 \neq k_4 \\ c_{1^k}^{(j)} c_{3^k}^{(j)} & \text{if } k_1 \neq k_3 \text{ and } k_2 = k_4 \\ 0 \end{cases}.$$  

otherwise.
Pairon operators of different types \( j \) always commute:
\[
[B^{(j)}, B^{(i)}] = 0 \quad \text{if} \ j \neq i,
\]
and
\[
\begin{align*}
n_1^{(j)} &= \epsilon_{k+q/2}^{(j)} c_{k+q/2}^{\dagger \prime} , \\
n_2^{(j)} &= \epsilon_{-k+q/2}^{(j)} c_{-k+q/2}^{\dagger \prime} ,
\end{align*}
\]
represent the number operators for “electrons” \( (j = 1) \) and “holes” \( (j = 2) \).

Let us now introduce the relative and net momenta \((k, q)\) such that
\[
\begin{align*}
k &\equiv (k_1 - k_2)/2 \\
q &\equiv k_1 + k_2.
\end{align*}
\]
Alternatively we can represent pairon annihilation operators by
\[
\begin{align*}
B^{(1)}_k &\equiv B^{(1)}_{k_1 k_2} \equiv \sum \epsilon_{-k+q/2}^{(1)} c_{-k+q/2}^{\dagger \prime} , \\
B^{(2)}_k &\equiv \sum \epsilon_{k+q/2}^{(2)} c_{k+q/2}^{\dagger \prime} .
\end{align*}
\]
The prime on \( B \) will be dropped hereafter. In the \((k, q)\) representation the commutation relations are re-expressed as
\[
\begin{align*}
[B^{(j)}_{kq}, B^{(i)}_{k'q'}] &\equiv 0, \\
[B^{(j)}_{kq}, B^{(i)}_{k'q'}]^2 &\equiv 0,
\end{align*}
\]
\[
\begin{align*}
&\left\{ (1 - \epsilon_{k+q/2}^{(j)} n_{-k+q/2}^{\prime}) \delta_{ji} \right. \\
&\text{if} \ k = k' \text{ and} \ q = q', \\
&\epsilon^{(j)}_{k+q/2} c_{k+q/2}^{\dagger \prime} \delta_{ji} \\
&\text{if} \ k + q/2 = k' + q'/2 \text{ and} \ -k + q'/2, \\
&\left. \epsilon^{(j)}_{k+q/2} c_{k+q/2}^{\dagger \prime} \delta_{ji} \right. \\
&\text{if} \ k + q/2 \neq k' + q'/2 \text{ and} \ -k + q'/2, \\
&\left. \epsilon^{(j)}_{k+q/2} c_{k+q/2}^{\dagger \prime} \delta_{ji} \right. \\
&\text{if} \ -k + q'/2, \\
&\text{otherwise}.
\end{align*}
\]

Using the new notations, we can write the full Hamiltonian as
\[
H = \sum_{k,s} \varepsilon^{(1)}_k n_{k,s} + \sum_{k,s} \varepsilon^{(2)}_k n_{-k,s} \\
- \sum_{k} \sum_{q} \sum_{k'} \sum_{q'} v_0 \left[ B^{(1)}_{kq} B^{(1)}_{k'q'} + B^{(1)}_{kq} B^{(2)}_{k'q'} + \\
B^{(2)}_{kq} B^{(1)}_{k'q'} + B^{(2)}_{kq} B^{(2)}_{k'q'} \right].
\]

This is the full Hamiltonian for the system, which can describe moving pairons as well as stationary pairons. Here, the prime on the summations indicates the restriction arising from the phonon exchange attraction, see below. The connection with BCS Hamiltonian \([16]\) will be discussed in Sec. \([VI]\).

\section{MOVING PAIRONS}

The phonon exchange attraction is in action for any pair of electrons near the Fermi surface. In general the bound pair has a net momentum, and hence it moves. The energy \( w_q \) of a moving pairon can be obtained from:
\[
w_q a(k, q) = \varepsilon(\{k + q/2\}) + \varepsilon(\{-k + q/2\}) - w_q > 0. \tag{44}
\]
Rearranging the terms in Eq. \((42)\) and dividing by \(\varepsilon(\{k + q/2\}) + \varepsilon(\{-k + q/2\}) - w_q\), we obtain
\[
a(k, q) = [\varepsilon(\{k + q/2\}) + \varepsilon(\{-k + q/2\}) - w_q]^{-1} C(q), \tag{45}
\]
where
\[
C(q) \equiv \frac{v_0}{(2\pi\hbar)^2} \int d^2 k' a(k', q), \tag{46}
\]
which is \( k \)-independent.

Introducing Eq. \((45)\) in Eq. \((42)\), and dropping the common factor \(C(q)\), we obtain
\[
1 = \frac{v_0}{(2\pi\hbar)^2} \int d^3 k \varepsilon(\{k + q/2\}) + \varepsilon(\{-k + q/2\}) + |w_q|^{-1}. \tag{47}
\]
We now assume a free electron moving in 3D. The Fermi surface is a sphere of the radius (momentum)
\[
k_F \equiv (2m_1\varepsilon_F)^{1/2}, \tag{48}
\]
where \(m_1\) represents the effective mass of an electron. The energy \(\varepsilon(|k|)\) is given by
\[
\varepsilon(|k|) \equiv \varepsilon_k = \frac{k^2 - k_F^2}{2m_1}. \tag{49}
\]
After performing the integration and taking the small-$q$ and small-$k_F$ limits, we obtain

$$w_q = w_0 + \frac{v_F}{2}q,$$

where the pairon ground-state energy $w_0$ is given by

$$w_0 = \frac{-2\hbar\omega_D}{\exp(2/v_0N(0)) - 1}.$$  

As expected, the zero-momentum pairon has the lowest energy $w_0$. The excitation energy is continuous with no energy gap. Equation (52) was first obtained by Cooper (unpublished), and it is recorded in Schrieffer’s book [22], Eq. (2.15). The energy $w_q$ increases linearly with momentum (magnitude) $q$ for small $q$. This behavior arises from the fact that the density of states is strongly reduced with the increasing momentum $q$ and dominates the $q^2$ increase of the kinetic energy. The linear dispersion relation means that a pairon moves like a massless particle with a common speed $v_F/2$. This relation plays a vital role in the B-E condensation of pairons (see next section).

Such a linear energy-momentum relation is valid for pairons moving in any dimension (D). However, the coefficients slightly depend on the dimensions; in fact

$$c/v_F = 1/2 \text{ and } 2/\pi \text{ for 3D and 2D, respectively.}$$

## VI. THE BOSE-EINSTEIN CONDENSATION OF PAIRONS

In Sec. [IV] we saw that the pair operators $(B, B^\dagger)$ appearing in the full Hamiltonian $H$ in Eq. (11) satisfy rather complicated commutator relations in Eqs. (39) and (40). In particular part of Eq. (39)

$$[B_{k_0j}^2] \equiv [b_k^\dagger]^2 = \left[\frac{\epsilon_{k_1}^j}{\epsilon_{k_1}}\epsilon_{k_2}^j\epsilon_{k_2}\right]^2 = 0$$

reflect the fermionic natures of the constituting electrons. Here, $B_{k_0j}^j = b_k^j$ represents creation operator for zero momentum pairons. BCS [16] studied the ground-state of a superconductor, starting with the reduced Hamiltonian $H_0$, which is obtained from the Hamiltonian $H$ in Eq. (11) by retaining the zero momentum pairons with $q = 0$, written in terms of $b$ by letting $B_{k_0j}^j = b_k^j$,

$$H_0 = \sum_k 2\epsilon_{k}^{(1)}b_k^{(1)\dagger}b_k^{(1)} + \sum_k 2\epsilon_{k}^{(2)}b_k^{(2)\dagger}b_k^{(2)} - \sum_k \sum_k' v_0\left[b_k^{(1)\dagger}b_k^{(1)} + b_k^{(1)\dagger}b_k^{(2)} + b_k^{(2)\dagger}b_k^{(2)} + b_k^{(2)\dagger}b_k^{(2)\dagger}\right].$$

Here, we expressed the “electron” and “hole” kinetic energies in terms of pairon operators. The reduced Hamiltonian $H_0$ is bilinear in pairon operators $(b, b^\dagger)$, and can be diagonalized exactly. BCS obtained the ground-state energy $E_0$ as

$$E_0 = \hbar\omega_D N(0)v_0,$$

where $N(0)$ is the density of states at the Fermi energy. The $w_0$ is the ground-state energy of the pairon, see Eq. (53). Equation (58) means simply that the ground state energy equals the numbers of pairons times the ground-state energy $w_0$ of the pairon. Our Hamiltonian $H$ in Eq. (11) is reduced to the original BCS Hamiltonian (see Ref. [16], Eq. (24)). There is an important difference in the definition of “electron” and “hole” here. BCS called the quasi-electron whose energy is higher (lower) than the Fermi energy $v_F$, the “electron” (“hole”). In our theory the “electrons” (“holes”) are defined as quasiparticles generated above (below) the Fermi energy and circulates counterclockwise (clockwise) viewed from the tip of an external magnetic field vector $\mathbf{B}$. They are generated, depending on the energy contour curvature signs. For example, only “electrons” (“holes”) are generated for
a circular Fermi surface with negative (positive) curvature whose inside (outside) is filled with electrons. Since the phonon has no charge, the phonon exchange cannot change the net charge. The pairing interaction terms in Eq. (11) conserve the charge. The term $-v_0 B_{kq}^{(1)\dagger} B_{kq}^{(1)}$, where $v_0 \equiv |V_0 V_0^*| (\hbar \omega_0 A)^{-1}$, $A$ = sample area, generates a transition in the “electron” states. Similarly, the exchange of a phonon generates a transition in the “hole” states represented by $-v_0 B_{kq}^{(2)\dagger} B_{kq}^{(2)}$. The phonon exchange can also pair-create or pair-annihilate “electron” (“hole”) pairons, and the effects of these processes are represented by $-v_0 B_{kq}^{(1)\dagger} B_{kq}^{(2)}$, as shown in Feynman diagrams in Figs. 5(a) and 5(b). At 0 K the system must have equal numbers of $- (+)$ zero-momentum (ground) pairons.

To describe a supercurrent, we must introduce moving pairons. We now show that the center-of-masses of the pairons move as bosons. That is, the number operator of pairons having net momentum $\mathbf{q}$

$$n_\mathbf{q} \equiv \sum_{\mathbf{k}} n_{\mathbf{kq}} = \sum_{\mathbf{k}} B_{\mathbf{kq}}^{\dagger} B_{\mathbf{kq}}$$

have the eigenvalues

$$n'_\mathbf{q} = 0, 1, 2, \ldots.$$  

The number operator for the pairons in the state $(\mathbf{k}, \mathbf{q})$ is

$$n_{\mathbf{kq}} \equiv B_{\mathbf{kq}}^{\dagger} B_{\mathbf{kq}} = c_{\mathbf{k}+\mathbf{q}/2}^{\dagger} c_{\mathbf{q}} - c_{\mathbf{q}}^{\dagger} c_{\mathbf{k}+\mathbf{q}/2},$$

where we omitted the spin indices. Its eigenvalues are limited to zero or one:

$$n'_{\mathbf{kq}} = 0 \text{ or } 1.$$  

To explicitly see this property in Eq. (60), we introduce

$$B_{\mathbf{q}} \equiv \sum_{\mathbf{k}} B_{\mathbf{kq}}$$

and obtain

$$[B_{\mathbf{q}}, n_{\mathbf{q}}] = \sum_{\mathbf{k}} \left( 1 - n_{\mathbf{k}+\mathbf{q}/2} - n_{\mathbf{q}-\mathbf{k}/2} \right) B_{\mathbf{kq}} = B_{\mathbf{q}}.$$  

$$[n_{\mathbf{q}}, B_{\mathbf{q}}^{\dagger}] = B_{\mathbf{q}}.$$  

Although the occupation number $n_{\mathbf{q}}$ is not connected with $B_{\mathbf{q}}$ as $n_{\mathbf{q}} \neq B_{\mathbf{q}}^{\dagger} B_{\mathbf{q}}$, the eigenvalues $n_{\mathbf{q}}$ of $n_{\mathbf{q}}$ satisfying Eq. (60) can be shown straightforwardly to yield

$$n'_\mathbf{q} = 0, 1, 2, \ldots.$$  

with the eigenstates

$$|0\rangle, |1\rangle = B_{\mathbf{q}}|0\rangle, \quad |2\rangle = B_{\mathbf{q}}^{\dagger} B_{\mathbf{q}}|0\rangle, \ldots.$$  

In summary, pairons with both $\mathbf{k}$ and $\mathbf{q}$ specified are subject to the Pauli exclusion principle, see Eq. (62). Yet, the occupation numbers $n'_{\mathbf{q}}$ of pairons having a CM momentum $\mathbf{q}$ are $0, 1, 2, \ldots$.

The most important signature of many bosons is the Bose-Einstein Condensation (BEC). Earlier we showed that the pairon moves in 2D with the linear dispersion relation, see (53):

$$w_p = w_0 + (2/\pi) v_F p \equiv w_0 + c p,$$

where we designated the pairon net momentum (magnitude) by the more familiar $p$ rather than $q$.

Let us consider a 2D system of free bosons having a linear dispersion relation: $\varepsilon = c p$, $c = (2/\pi) v_F$. The number of bosons, $N$, and the Bose distribution function

$$f_B(\varepsilon; \beta, \mu) \equiv \frac{1}{e^{\beta(\varepsilon-\mu)}-1} \equiv f_B(\varepsilon) > 0$$

are related by

$$N = \sum_{\mathbf{p}} f_B(\varepsilon_{\mathbf{p}}, \beta, \mu) = N_0 + \sum_{\varepsilon_p > 0} f_B(\varepsilon_p),$$

where $\mu$ is the chemical potential, $\beta = (k_B T)^{-1}$, and $N_0 \equiv (e^{-\beta \mu} - 1)^{-1}$.

is the number of zero-momentum bosons. The prime on the summation in Eq. (60) indicates the omission of the zero-momentum state. For notational convenience, we write

$$\varepsilon = c p = (2/\pi) v_F p > 0.$$

We divide Eq. (63) by the normalization area $L^2$, and take the bulk limit:

$$N \to \infty, \quad L \to \infty \quad \text{while} \quad NL^{-2} \equiv n.$$

We then obtain

$$n - n_0 \equiv \frac{1}{(2\pi \hbar)^2} \int d^2 p f_B(\varepsilon),$$

where $n_0 \equiv N_0/L^2$ is the number density of zero-momentum bosons and $n$ the total boson density. After performing the angular integration and changing integration variables, we obtain from Eq. (73):

$$2\pi \hbar^2 c^2 \beta^2 (n - n_0) = \int_0^\infty dx \frac{x}{\lambda^{-1} e^x - 1}$$

$$(x \equiv \beta \varepsilon),$$

where the fugacity

$$\lambda \equiv e^{\beta \mu} (< 1),$$

is less than unity for all temperatures. After expanding the integrand in Eq. (74) in powers of $\lambda e^{-x} (< 1)$, and carrying out the $x$-integration, we obtain

$$n_x \equiv n - n_0 = \frac{k_B^2 T^2 \phi_2(\lambda)}{2\pi \hbar^2 c^2},$$

(76)
zero momentum bosons, theorem. \[24\], and hence they are not subject to Hohenberg's theorem (no long range order in 2D). But this temperature \(T > T_\text{c}\) for condensed region: \(\lambda\) smaller than \(1\), in the weak coupling limit. The electron energy gap \(\Delta(T)\) and the pairon ground-state energy \(u_0\) both depend on the phonon-exchange coupling energy parameter \(v_0\), which appears in the starting Hamiltonian \(H\) in Eq. \(41\). The energy \(u_0\) is negative (bound-state energy). Hence, this \(u_0\) cannot be obtained by the perturbation theory. The connection between \(u_0\) and \(v_0\) is very complicated. This makes it difficult to discuss the critical temperature \(T_\text{c}\) based on the BCS relation \(81\). Unlike the BCS formula, formula \(79\) is directly connected with the measurable quantities: the pairon density \(n_0\) and the Fermi speed \(v_F\).

We emphasize here that both formulas \(79\) and \(81\) were derived, starting with the Hamiltonian \(H\) in Eq. \(41\) and following statistical mechanical calculations, see the reference \[26\] for details.

\[\phi_2(\lambda) \equiv \sum_{k=1}^{\infty} \frac{\lambda^k}{k!^2} \quad (0 \leq \lambda \leq 1). \tag{77}\]

Equation \(76\) gives a relation among \(\lambda\), \(n\), and \(T\).

The function \(\phi_2(\lambda)\) monotonically increases from zero to the maximum value

\[\phi_2(1) = 1.645 \tag{78}\]
as \(\lambda\) is raised from zero to one. In the low-temperature limit, \(\lambda = 1\), \(\phi_2(\lambda) = \phi_2(1) = 1.645\), and the density of excited bosons, \(n_x\), varies as \(T^2\) as seen from Eq. \(76\). This temperature behavior of \(n_x\) persists as long as the right-hand-side (r.h.s.) of Eq. \(76\) is smaller than \(n\); the critical temperature \(T_\text{c}\) occurs at \(n_c = k_B T_\text{c}^2 \phi_2(1)/2\pi \hbar^2 c^2\). Solving this, we obtain

\[k_B T_\text{c} = 1.954 h c n^{1/2} \quad (= 1.24 h v_F n^{1/2}). \tag{79}\]

The BEC of pairons moving in 2D occurs at a finite temperature. This appears to contradict with Hohenberg's theorem (no long range order in 2D). But this theorem is proved under the assumption of the f-sum rule arising from the mass conservation. The pairons move massless with the linear dispersion relation [see Eq. \(71\)], and hence they are not subject to Hohenberg's theorem. \[24\]

If the temperature is raised beyond \(T_\text{c}\), the density of zero momentum bosons, \(n_0\), becomes vanishingly small, and the fugacity \(\lambda\) can be determined from

\[n = \frac{k_B T_\text{c}^2 \phi_2(\lambda)}{2\pi \hbar^2 c^2}, \quad T > T_\text{c}. \tag{80}\]

In summary, the fugacity \(\lambda\) is equal to unity in the condensed region: \(T < T_\text{c}\), and it becomes smaller than unity for \(T > T_\text{c}\), where its value is determined from Eq. \(80\).

Formula \(79\) for the critical temperature \(T_\text{c}\) is distinct from the famous BCS formula

\[3.53 k_B T_\text{c} = 2 \Delta_0, \tag{81}\]

where \(\Delta_0\) is the zero temperature electron energy gap in the weak coupling limit. The electron energy gap.
running in the wall. The differential conductance \(dI/dV\) is very small and nearly constant (superconducting) for \(V < 10\) mV in the HRC sample, see the lower panel in Fig. [1]. We stress that if the ballistic electron model [2] is adopted, then the scatterings by phonons cannot be discussed. The non-linear IV curves below 150 K mean that the carbon wall is superconducting. Thus, the clearly visible temperature effects for both LRC and HRC samples arise from the phonon scattering. We assumed that the system is superconducting below \(\sim 150\) K. The ZBA arises only from the superconducting state. The superconducting critical temperature \(T_c\) must then be higher than 150 K. An experimental check of \(T_c\) is highly desirable.

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