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Theory of superconductivity. New formula for the critical temperature

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ABSTRACT. Based on the BCS Hamiltonian, the normal-to-super phase transition is investigated, approaching the critical temperature T_c from the high temperature side. Non-zero momentum Cooper pairs, that is, pairs of electrons (holes) with antiparallel spins and nearly opposite momenta above T_c in the bulk limit, are shown to move like free bosons with the energy (ϵ)–momentum (p) relation $\epsilon = \frac{1}{2}v_F p$, where v_F represents the Fermi velocity. The system of free Cooper pairs undergoes a phase transition of the second order at the critical temperature T_c given by $k_B T_c = 1.00856\hbar v_F n^{1/3}$, where n is the number density of Cooper pairs. The ratio of the jump of the heat capacity, ΔC, to the maximum heat capacity, C_s, is a universal constant: $\Delta C/C_s = 0.60874$; this number is close to the universal constant 0.588 obtained by the finite-temperature BCS theory.

RESUMEN. Haciendo uso del hamiltoniano BCS, se investiga la transición de fase normal-superconductora, aproximando la temperatura crítica T_c del lado de alta temperatura. Se muestra que pares de Cooper de momento diferente de cero, esto es pares de electrones (hoyos) con espines antiparalelos y momentos casi opuestos arriba de la temperatura T_c y en el límite macroscópico, tienen movimientos de bosones libres con energía (ϵ) y momento (p) en una relación $\epsilon = \frac{1}{2}v_F p$, donde v_F representa la velocidad de Fermi. El sistema de pares de Cooper libres, sufre una transición de fase de segundo orden a la temperatura T_c dada por $k_B T_c = 1.00856\hbar v_F n^{1/3}$, donde n es la densidad de pares de Cooper. El cociente del salto de la capacidad calorífica ΔC al máximo valor de la capacidad C_s, es una constante universal: $\Delta C/C_s = 0.60874$; este número es cercano a la constante universal 0.588 que se obtiene usando la teoría BCS a temperatura finita.

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1. INTRODUCTION

In the classic paper in 1957, Bardeen, Cooper and Schrieffer (BCS) [1] proposed a microscopic theory of superconductivity by constructing the super condensate of zero-momentum Cooper pairs. Most of the striking properties of the low-T_c ($T_c < 25$ K) superconductors were successfully accounted for by this theory based on the BCS Hamiltonian (11).

Subsequently, several many-body techniques have been applied to calculate the thermodynamic properties of a system characterized by the BCS Hamiltonian [2,3]. All of these theories confirm the original BCS description of the ground-state condensate in terms of zero-momentum Cooper pairs at 0 K. The theoretical treatments of the normal-to-super transition, where the critical temperature T_c is regarded as the point at which the energy gap Δ vanishes, contain approximations. In particular, the second-order phase transition obtained in these theories are thought to arise from the mean-field theoretical methods employed rather than from the rigorous treatment.

In the present work, we shall present yet another microscopic theory, starting with the BCS Hamiltonian (11) but looking at the normal-to-super transition from the high temperature side. A special advantage of such a theory is that one can deal with the phase transition in terms of the elementary excitations (moving Cooper pairs) in the normal states [4]. It is shown that the normal-to-super transition is a second-order phase transition associated with the B-E condensation [5] of non-zero momentum Cooper pairs having the linear energy-momentum relation

$$\epsilon = \tfrac{1}{2} v_F p, \quad (\tfrac{1}{2} m v_F^2 \equiv \epsilon_F = \text{Fermi energy}); \tag{1}$$

a relation derived by Cooper and recorded in Ref. [2] (pp. 28–33). The critical temperature T_c is given by [6]

$$k_B T_c = \tfrac{1}{2}(\pi^2 \hbar^3 v_F^3 n / 1.20257)^{1/3} = 1.00856 \hbar v_F n^{1/3}. \tag{2}$$

where n is the number density of Cooper pairs. The ratio of the jump of the heat capacity, ΔC, to the maximum heat capacity, C_s, is a universal constant: $\Delta C / C_s = 0.60874$; this number is close to the universal constant 0.588 obtained by the finite-temperature BCS theory.

2. THE B-E CONDENSATION OF FREE BOSONS WITH $\epsilon = \frac{1}{2} v_F p$

The numbers of bosons, N, and the Bose distribution function,

$$f(\epsilon; \beta, \mu) \equiv \left[e^{\beta(\epsilon - \mu)} - 1 \right]^{-1} \quad (> 0), \tag{3}$$

are related by

$$N = \sum_{\substack{\text{momentum} \\ \text{states}}} f(\epsilon_p; \beta, \mu) = N_0 + \sum_{\substack{\text{states} \\ \epsilon_p > 0}} f(\epsilon), \tag{4}$$

where $\beta \equiv (k_B T)^{-1}$ and μ are respectively the reciprocal temperature and the chemical potential; and N_0 is the number of zero-momentum bosons.

Let us consider free massless bosons having the energy-momentum relation (1) and moving in 3D. In the bulk limit

$$N \to \infty, \qquad \Omega \to \infty \text{ while } n \equiv N/\Omega = \text{finite}, \tag{5}$$

where Ω represents the volume, the normalization condition (4) can be reduced to

$$\begin{aligned} n_x \equiv n - n_0 &= (2\pi\hbar)^{-3} \int d^3p\, f(\epsilon; T, \mu) \\ &= \tfrac{1}{2}\left(\pi^2\hbar^3 v_F^3\right)^{-1} k_B^3 T^3 \phi_3(\lambda), \end{aligned} \tag{6}$$

where

$$\phi_m(\lambda) \equiv \sum_{k=1}^{\infty} \frac{\lambda^k}{k^m}, \tag{7}$$

and $\lambda = \exp(\beta\mu)$ is the fugacity, which is less than unity for the whole temperature range $(0, \infty)$.

The functions $\phi_m(\lambda)$, $m > 1$, are monotonically growing functions of λ, $0 < \lambda < 1$, and have the greatest values at $\lambda = 1$

$$\begin{aligned} &\phi_2(1) = 1.64493, \quad \phi_3(1) = 1.202057, \\ &\phi_4(1) = 1.082323, \quad \left[\phi_m(1) = \zeta(m) = \text{Riemann zeta function}\right]. \end{aligned} \tag{8}$$

Study of Eq. (6) indicates that: (a) the fugacity λ is unity for the degenerate region: $T < T_c$, where T_c is defined by (2); and (b) λ becomes less than unity for the non-degenerate region: $T > T_c$, where the value of λ can be determined from Eq. (6) with $n_x = n$.

The internal energy density u can be calculated from

$$u \equiv (2\pi\hbar)^{-3} \int d^3p\, \epsilon f(\epsilon) = 3nk_B \frac{T^4}{T_c^3} \frac{\phi_4(\lambda)}{\phi_3(1)}. \tag{9}$$

The molar heat capacity C_V defined by $C_V \equiv R(nk_B)^{-1} \frac{\partial u(T,V)}{\partial T}$, where R is the gas constant, can be represented by [6]

$$C_V = \begin{cases} 12R\left(\dfrac{T}{T_c}\right)^3 \dfrac{\phi_4(1)}{\phi_3(1)} = 10.8047R\left(\dfrac{T}{T_c}\right)^3, & \text{if } T < T_c; \\[2ex] C_V = 12R\left(\dfrac{T}{T_c}\right)^3 \dfrac{\phi_4(\lambda)}{\phi_3(1)} - 9R\dfrac{\phi_3(\lambda)}{\phi_2(\lambda)}, & \text{if } T < T_c. \end{cases} \tag{10}$$

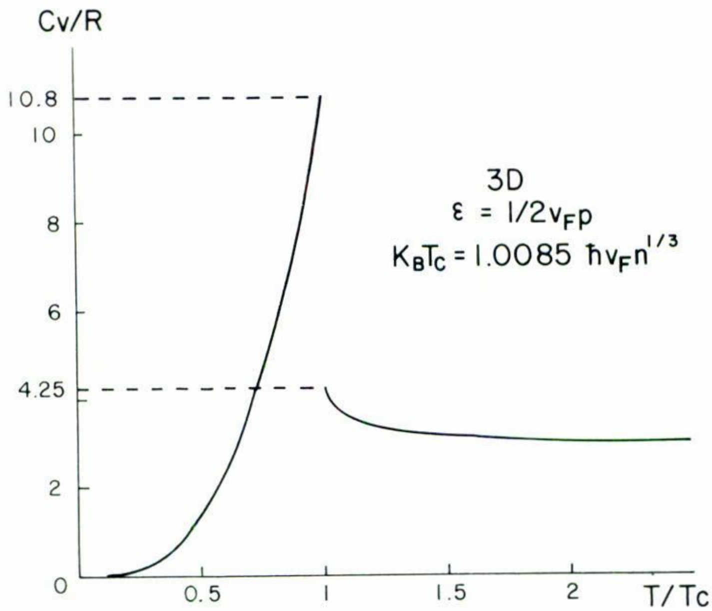

FIGURE 1. The molar heat capacity C_V for bosons with $\epsilon = cp$ $(= \frac{1}{2}v_F p)$ and moving in 3D rises like T^3, and reaches 10.80 R at the transition temperature $T_c = 2.017\hbar c n^{1/3} k_B^{-1}$; it then drops off abruptly by $6.58R$ and approaches the high-teperature-limit value $3R$.

At the critical temperature T_c, the C_V has a discontinuous jump equal to $9R\phi_3(1)/\phi_2(1) = 6.5769\ R$. The temperature behavior of C_V is shown in Fig. 1. Thus, the B-E condensation is characterized by the second-order phase transition.

3. NONZERO MOMENTUM COOPER PAIRS ABOVE T_c

The basic assumptions of the BCS microscopic theory [1,2] are that: (i) in spite of the Coulombic electron-electron interaction there exists a well-defined Fermi energy ϵ_F for the normal state of a metal, as described by the Fermi liquid theory of Landau [7]; and (ii) the electron-phonon interaction generates an attraction between electrons near the Fermi energy surface [8]. Under these two assumptions the BCS model Hamiltonian H may be written in the form

$$H = \sum_{\vec{k}} \sum_{\epsilon_k^s > 0} \epsilon_k c_{\vec{k}s}^\dagger c_{\vec{k}s} + \sum_{\vec{k}} \sum_{\epsilon_k^s < 0} |\epsilon_k| c_{\vec{k}s} c_{\vec{k}s}^\dagger$$

$$+ \frac{1}{2} \sum_{\vec{k}_1} \cdots \sum_{\vec{k}_4} \sum_{s} \sum_{s'} \langle 12|V|34\rangle c_{1s}^\dagger, c_{2s}^\dagger, c_{4s}, c_{3s}, \tag{11}$$

where $\epsilon_{k_1} \equiv (2M)^{-1} k_1^2 - \epsilon_F \equiv \epsilon_1$ is the kinetic energy of the Bloch electron measured relative to the Fermi energy ϵ_F, and $c_{\vec{k}_1 s}^\dagger \equiv c_{1s}^\dagger$ (c_{1s}) are creation (annihilation) operators satisfying the Fermi commutation relations

$$\begin{aligned}
&\left\{c_{\vec{k}s},\, c^{\dagger}_{\vec{k}'s'}\right\} \equiv c_{\vec{k}s}c^{\dagger}_{\vec{k}'s'} + c^{\dagger}_{\vec{k}'s'}c_{\vec{k}s} = \delta_{\vec{k},\vec{k}'}\delta_{s,s'} \\
&\left(c_{\vec{k}s},\, c_{\vec{k}'s'}\right) = 0.
\end{aligned} \tag{12}$$

The matrix element $\langle 12|V|34\rangle \equiv \langle \vec{k}_1\vec{k}_2|V|\vec{k}_3\vec{k}_4\rangle$ denotes the effective interaction arising from virtual exchange of phonons between the electrons. and this element has an attractive interaction character represented by

$$\langle 12|V|34\rangle = \begin{cases} -V_0\Omega^{-1}\delta_{\vec{k}_1+\vec{k}_2,\vec{k}_3+\vec{k}_4} & \text{if } |\epsilon_i| < \hbar\omega_c, \\ 0 & \text{otherwise.} \end{cases} \tag{13}$$

By introducing (iii) the pairing approximation in which electrons with opposite momenta and spins, $(\vec{k}\uparrow, -\vec{k}\downarrow)$, are paired, BCS constructed a many-electron ground state (condensate).

In the present work, we shall assume (i) and (ii), and modify (iii) to consider the electron-pairs of opposite spins but having the net momenta not necessarily equal to zero. We shall call these pairs the Cooper pairs because Cooper examined them first in his original work [4].

Let us introduce the bulk limit [see (5)]. In this limit, the k-vectors (momenta) form a continuous spectrum. Then it is convenient to introduce distribution functions (or densities). For example, the momentum distribution function $n_s(\vec{k})$ is defined through

$$n_s(\vec{k})\, d^3k\Omega(2\pi\hbar)^{-3} = \text{the number of electrons with spin } s \text{ in } d^3k \text{ at } \vec{k} \tag{14}$$

The quantum operator corresponding to $n_s(\vec{k})$ can be expressed (see Appendix) by

$$n_s(\vec{k}) \equiv c^{\dagger}_s(\vec{k})c_s(\vec{k}), \tag{15}$$

where $c^{\dagger}_s(\vec{k})$ $[c_s(\vec{k})]$ are creation (annihilation) operators satisfying

$$\begin{aligned}
&\left\{c_s(\vec{k}),\, c^{\dagger}_{s'}(\vec{k}')\right\} = \delta^{(3)}(\vec{k}-\vec{k}')\delta_{ss'}, \\
&\left\{c_s(\vec{k}),\, c_{s'}(\vec{k}')\right\} = 0.
\end{aligned} \tag{16}$$

Our Hamiltonian defined by (11–13) conserves the net momentum

$$\vec{k}_1 + \vec{k}_2 = \vec{k}_3 + \vec{k}_4. \tag{17}$$

We now introduce the relative and center-of-mas momenta

$$\vec{k}_1 = \vec{k} + \tfrac{1}{2}\vec{q}, \qquad \vec{k}_2 = -\vec{k} + \tfrac{1}{2}\vec{q},$$
$$\vec{k}_3 = \vec{k}' + \tfrac{1}{2}\vec{q}', \qquad \vec{k}_4 = -\vec{k}' + \tfrac{1}{2}\vec{q}'. \tag{18}$$

The Cooper electron [hole]-pair will be defined as a pair of electrons which have opposite spins *and* have energies in the range $(0, \hbar\omega_c)[(-\hbar\omega_c, 0)]$. Second-quantized operators for the pair may be represented by

$$b^\dagger(\vec{k},\vec{q}) = c_\downarrow^\dagger(-\vec{k} + \tfrac{1}{2}\vec{q})c_\downarrow^\dagger(-\vec{k} + \tfrac{1}{2}\vec{q}), \qquad b(\vec{k},\vec{q}) = c_\downarrow(-\vec{k} + \tfrac{1}{2}\vec{q})c_\uparrow(\vec{k} + \tfrac{1}{2}\vec{q}),$$
$$\left|\epsilon_{\vec{k}+\frac{1}{2}\vec{q}}\right|, \quad \left|\epsilon_{-\vec{k}+\frac{1}{2}\vec{q}}\right| < \hbar\omega_c. \tag{19}$$

The commutation relations for these operators can be computed by using (16) and assuming (17). They are given by

$$\left[b(\vec{k},\, \vec{q}), b^\dagger(\vec{k}', \vec{q}')\right] \equiv b(\vec{k},\vec{q})b^\dagger(\vec{k}',\vec{q}') - b^\dagger(\vec{k}',\vec{q}')b(\vec{k},\vec{q})$$
$$= \delta^{(3)}(\vec{k} - \vec{k}')\delta^{(3)}(\vec{q} - \vec{q}') \tag{20a}$$

$$\left[b(\vec{k},\vec{q}),\, b(\vec{k}',\vec{q}')\right] = 0. \tag{20b}$$

It can further be shown (see Appendix) that

$$\left[b(\vec{k},\vec{q})\right]^2 = 0. \tag{21}$$

This is similar to

$$\left(B_{\vec{k},\vec{q}}\right)^2 = \left(c_{\vec{k}+\frac{1}{2}\vec{q}}\uparrow c_{-\vec{k}+\frac{1}{2}\vec{q}}\downarrow\right)^2 = 0, \tag{22}$$

which can be shown simply from (12), and which arises from the Pauli exclusion principle [the second of Eqs. (12)]. We stress that Eq. (21) does not invalidate Eqs. (20a) since a continuous function defined in the six-dimensional $k - q$ space cannot be influenced by the restriction on the function imposed at "planes" of lesser dimensions. Thus, the moving Cooper pair operators satisfy the Bose commutation relations (20). In other words moving Cooper pairs are bosons. This is to be contrasted with the case of zero-momentum or ground Cooper pairs. As emphasized by BCS [1], the quantum-state affiliated operator's for zero-momentum ($q = 0$) Cooper pairs are restricted by the condition (21), and therefore the ground Cooper pairs, which may form a supercondensate at 0 K, are neither bosons nor fermions.

Following Dirac [9], we introduce creation and annihilation operators for "electrons" and "holes", denoted by scripts 1 and 2 respectively, with the Fermi sea vacuum states $|\phi_j\rangle$

$$\begin{aligned} c_s^{(1)}(\vec{k}) &\equiv c_s(\vec{k}), & c_s^{(2)}(\vec{k}) &\equiv c_s^\dagger(\vec{k}), \\ c_s^{(1)}(\vec{k})|\phi_1\rangle &= 0, & c_s^{(2)}(\vec{k})|\phi_2\rangle &= 0, \\ n_s^{(1)}(\vec{k}) &= c_s^{(1)\dagger}(\vec{k})c_s^{(1)}(\vec{k}), & n_s^{(2)}(\vec{k}) &= c_s^{(2)\dagger}(\vec{k}) = c_s^{(2)}(\vec{k}), \\ \epsilon_k^{(1)} &\equiv \epsilon_k > 0, & \epsilon_k^{(2)} &\equiv -\epsilon_k > 0. \end{aligned} \tag{23}$$

In the bulk limit, the BCS Hamiltonian (11) per unit volume may be written as follows:

$$\begin{aligned} H = {} & \frac{1}{(2\pi\hbar)^3}\sum_s \int d^3k\, \epsilon_k^{(1)} n_s^{(1)}(\vec{k}) + \frac{1}{(2\pi\hbar)^3}\sum_s \int d^3k\, \epsilon_k^{(2)} n_s^{(2)}(\vec{k}) \\ & - (2\pi\hbar)^{-6}\int \cdots \int' d^3k\, d^3q\, d^3k'\, d^3q' \\ & \Big[V_{11} b_1(\vec{k}',\vec{q}')b_1^\dagger(\vec{k},\vec{q}) + V_{12} b_1(\vec{k}',\vec{q}')b_2(\vec{k},\vec{q}) \\ & + V_{21} b_2^\dagger(\vec{k}',\vec{q}')b_1^\dagger(\vec{k},\vec{q}) + V_{22} b_2^\dagger(\vec{k}',\vec{q}')b_2(\vec{k},\vec{q})\Big]\delta^{(3)}(\vec{q}-\vec{q}'), \end{aligned} \tag{24}$$

where b_j are pair annihilation operators defined by

$$\begin{aligned} b_1(\vec{k}',\vec{q})] &\equiv c_\downarrow^{(1)}(-\vec{k}+\tfrac{1}{2}\vec{q})c_\uparrow^{(1)}(\vec{k}+\tfrac{1}{2}\vec{q}), \\ b_2(\vec{k}',\vec{q})] &\equiv c_\uparrow^{(2)}(\vec{k}+\tfrac{1}{2}\vec{q})c_\downarrow^{(2)}(-\vec{k}+\tfrac{1}{2}\vec{q}) \end{aligned} \tag{25}$$

and the prime on the multiple integral means the restriction that all of kinetic energies: $\epsilon^{(j)}_{\vec{k}+\frac{1}{2}\vec{k}}$, $\epsilon^{(j)}_{-\vec{k}+\frac{1}{2}\vec{q}}$, $\epsilon^{(j)}_{\vec{k}'+\frac{1}{2}\vec{k}'}$, and $\epsilon^{(j)}_{-\vec{k}'+\frac{1}{2}\vec{q}}$ be in $(0, \hbar\omega_c)$. We stress that different correlation strengths V_{ij} are assumed for pairs (i,j).

The commutation relations for "electron" and "hole" pair operators can be worked out from (16), (23) and (25). They are given by

$$\begin{aligned} \big[b_j(\vec{k},\,\vec{q}), b_\ell^\dagger(\vec{k}',\vec{q}')\big] &= \delta^{(3)}(\vec{k}-\vec{k}')\delta^{(3)}(\vec{q}-\vec{q}')\delta_{j\ell}, \\ \big[b_j(\vec{k},\,\vec{q}), b_\ell(\vec{k}',\vec{q}')\big] &= 0. \end{aligned} \tag{26}$$

Using (24)–(26) we compute the commutator $[H, b_j^\dagger(\vec{k},\vec{q})]$ and obtain

$$\Big[H, b_1^\dagger(\vec{k},\vec{q})\Big] = \big(\epsilon^{(1)}_{\vec{k}+\frac{1}{2}\vec{q}} + \epsilon^{(1)}_{-\vec{k}+\frac{1}{2}\vec{q}}\big) b_1^\dagger(\vec{k},\vec{q}) - V_{11}(2\pi\hbar)^{-3}\int' d^3k'\, b_1^\dagger(\vec{k},\vec{q}) - V_{12}(2\pi\hbar)^{-3}\int' d^3k'\, b_2(\vec{k}',\vec{q}), \quad (27a)$$

$$\Big[H, b_2(\vec{k},\vec{q})\Big] = \big(\epsilon^{(2}_{\vec{k}+\frac{1}{2}\vec{q}} + \epsilon^{(2)}_{-\vec{k}+\frac{1}{2}\vec{q}}\big) b_2(\vec{k},\vec{q}) - V_{21}(2\pi\hbar)^{-3}\int' d^3k'\, b_1^\dagger(\vec{k}',\vec{q}) - V_{22}(2\pi\hbar)^{-3}\int' d^3k'\, b_2(\vec{k}',\vec{q}). \quad (27b)$$

Observe here that the net momentum $\vec{q}$ is a constant of motion, which arises from the momentum conservation (17). This means that once a Cooper pair is generated, it cannot be destroyed by the BCS interaction Hamiltonian. Thus, the stationary state of the system can be described in terms of independently moving Cooper pairs. The pair operators are coupled with independently moving Cooper pairs. The pair operators are coupled with respect to the other variable $\vec{k}$, meaning that the "wave functions" for the Cooper pairs are superpositions of the pair plane-wave functions. In the normal metal state above T_c we can use the Bloch (plane-) wave functions to reduce the operator Eqs. (27) to c-number equations.

First, we assume that a correlation exists among the electron-pairs only ($V_{12} = 0$). From (27a), we then obtain

$$W_q^{(1)} a_1(\vec{k},\vec{q}) = \Big(\epsilon^{(1)}_{\vec{k}+\frac{1}{2}\vec{q}} + \epsilon^{(1)}_{-\vec{k}+\frac{1}{2}\vec{q}}\Big) a_1(\vec{k},\vec{q}) - V_{11}(2\pi\hbar)^{-3}\int d^3k\, a_1(\vec{k}',\vec{q}), \quad (28)$$

where $W_q^{(1)}$ is the energy-eigenvalue and a_1 the Fourier-transform of the wave function for the electron pair, denoted by the superscript 1. Eq. (28) is identical with the original Cooper pair equation (Eq. (1) of Ref. [4]). The eigenvalue $W_q^{(1)}$ was worked out in Ref. [2], (p. 28–33) and it is given by

$$W_q^{(1)} = W_0^{(1)} + \tfrac{1}{2} v_F^{(1)} q, \quad v_F^{(1)} \equiv \left(\frac{2\epsilon_F}{m_1}\right)^{1/2}, \quad (29)$$

$$W_0^{(1)} \cong -2\hbar\omega_c \exp\left[-\frac{2}{V_{11}N(0)}\right], \quad (30)$$

where $N(0)$ is the density of single-electron states of one spin orientation evaluated at the Fermi surface. Thus, the pair excitation energy increases linearly with the momentum q

in the limit $q \to 0$ rather than quadratically. This behavior arises from the fact that the density of states is strongly reduced with the net momentum q, and this dominates the q^2 increase of kinetic energy for small q. A similar result is obtained for the case of the (hole-pair, hole-pair) correlation characterized by V_{22}. In summary, the electron and hole Cooper pairs are formed with the bound energies

$$W_q^{(j)} = W_0^{(j)} + \tfrac{1}{2} v_F^{(j)} q, \qquad j = 1, 2. \tag{31}$$

We shall go back to the general case in which $V_{ij} \neq 0$, $(i,j) = 1,2$. From (29) and (30), we obtain

$$\begin{aligned} W_q a_1(\vec{k}, \vec{q}) &= \left(\epsilon^{(1)}_{\vec{k}+\frac{1}{2}\vec{q}} + \epsilon^{(1)}_{-\vec{k}+\frac{1}{2}\vec{q}}\right) a_1(\vec{k}, \vec{q}) \\ &\quad - V_{11}(2\pi\hbar)^{-3} \int' d^3k'\, a_1(\vec{k}', \vec{q}) - V_{12}(2\pi\hbar)^{-3} \int' d^3k'\, a_2^*(\vec{k}', \vec{q}), \\ W_q a_2^*(\vec{k}, \vec{q}) &= \left(\epsilon^{(2)}_{\vec{k}+\frac{1}{2}\vec{q}} + \epsilon^{(2)}_{-\vec{k}+\frac{1}{2}\vec{q}}\right) a_2^*(\vec{k}, \vec{q}) \\ &\quad - V_{22}(2\pi\hbar)^{-3} \int' d^3k'\, a_2^*(\vec{k}, \vec{q}) - V_{21}(2\pi\hbar)^{-3} \int' d^3k'\, a_1(\vec{k}, \vec{q}). \end{aligned} \tag{32}$$

These equations indicate that a general Cooper pair wave function is a superposition of those pair-plane-wave functions describing the electron-pairs and hole-pairs.

Let us now consider a special case in which there is a symmetry between electron and hole such that: (a) both particles have the same effective mass and therefore they have the same excitation energy when their momenta (magnitude) is different from the Fermi momentum p_F by a fixed amount; and (b) the correlation-interaction strengths are the same between and among the species:

$$V_{ij} = V_0. \tag{33}$$

In fact, this is the case which was considered originally by BCS and has been adopted routinely by the subsequent investigators. In this special case, Eqs. (32) becomes identical with Eq. (28) except for the extension of the integration domain of correlation. Thus, the eigenvalue W_q is given by

$$W_q = W_0 + \tfrac{1}{2} v_F q, \tag{34}$$

$$W_0 \cong -2\hbar\omega_c \exp\left[-\frac{1}{V_0 N(0)}\right]. \tag{35}$$

It should be noticed that the arguments of the exponential factors in (30) and (35) are different by the factor 2 due to the fact that the domains of correlation are different by this factor. The new binding energy W_0 is greater than $W_0^{(1)}$ $(= W_0^{(2)})$ by this reason.

As temperature is lowered toward 0 K, the number of the Cooper pairs should increase because of the binding energy W_0. But because the Cooper pairs are bosons, the number density of the excited Cooper pairs, n_x, have the upper limits [see Eq. (6)] for a given temperature T. Thus, the B-E condensation must occur at the critical temperature T_c, given by (2).

At the critical temperature T_c, the thermodynamic properties of the Cooper pairs should exhibit singular behaviors characteristic of a phase transition of the second oder. In particular, the heat capacity C must have a jump ΔC as pictured in Fig. 1. The ratio of this jump ΔC to the maximum heat capacity C_s at T_c can be computed from (10), yielding

$$\frac{\Delta C}{C_s} = \frac{6.5769\ R}{10.8047\ R} = 0.60874, \tag{36}$$

and it is a universal constant (number).

The BCS theory, starting with the same Hamiltonian (11), treats the much more formidable problem of a many-electron condensate at 0 K and above up to the critical temperature T_c. This T_c is determined from the fact that the energy gap Δ, which is a function of zero-momentum Cooper pair density, should vanish at T_c. The elementary excitations above the condensate generate the heat capacity of the superconductor. the heat capacity calculated from the BCS theory exhibits a second-order phase transition at T_c, and the ratio $\Delta C/C_s$ is approximately given by [2]

$$\left(\frac{\Delta C}{C_s}\right)_{\rm BCS} = 0.588. \tag{37}$$

Note that the two numbers in (36) and (37) are quite close to each other. The small difference, we believe, is due to the approximations involved in the finite-temperature BCS theory near T_c.

Experimentally, the low-T_c ($T_c < 25$ K) superconductors exhibit second-order phase transitions, and most of them confirm the universal law (37) or (36) within tens of percents. This has been considered as one of the great successes of the BCS theory.

The present theory treats the thermodynamic behavior of the Cooper pairs near T_c from the high temperature side. Below T_c, the energy-momentum ($W_q - q$) relation changes from (34) to a new one involving an energy gap $\Delta(T)$ because of the presence of the BCS condensate. However at the immediate vicinity of T_c, where Δ is zero, the energy-momentum relation should be of the form (34). Then, the temperature behavior of the heat capacity C near T_c should be described by (10), and therefore C should decrease like T^3 as T is reduced

$$C = 10.804R(T/T_c)^3, \qquad 1 - T/T_c \ll 1. \tag{38}$$

This T^3-law is in a good agreement with the experimental data [10].

3. SUMMARY AND DISCUSSIONS

In the present work, the thermodynamic properties of a system characterized by the BCS Hamiltonian (11) are investigated by looking at the normal-to-super transition from the high temperature side. It is established that: (a) non-zero momentum Cooper pairs above the critical temperature T_c move like free bosons in the bulk limit; and (b) the Cooper pairs with the energy-momentum relation $\epsilon = \frac{1}{2}v_F p$ undergoes a phase-transition of the second order with the critical temperature given by (2).

The theory by means of a distribution function is valid only if the occupation number is finite int he whole domain of definition. Below T_c, (the region outside of our main concern here), the number of the Cooper pairs occupying the zero-momentum pair-state becomes indefinitely large in the bulk limit. Therefore, the zero-momentum pairs must be treated with a great care as first pointed out by Einstein [5], [see Eqs. (4) and (6), where the number (density) of zero momentum bosons, $N_0(n_0)$, are treated separately from the rest]. BCS [1,2] stressed this fact and constructed the ground-state wave function in terms of zero-momentum Cooper pairs, which are not bosons because of (22). But non-zero momentum Cooper pairs above T_c can be treated as bosons. Thus, there are no contradiction between the BCS treatment of the zero-momentum condensate and the present treatment of the B-E condensation of non-zero-momentum Cooper pairs.

One of the significant findings in our theory is that the critical temperature T_c is connected with the density of the Cooper pairs, n, as represented by (22). In fact, this equation gives a new independent formula for T_c in addition to the celebrated BCS formula [1]

$$k_B T_c = 1.14\hbar\omega_c \exp\left[-\frac{1}{V_0 N(0)}\right]. \tag{39}$$

By expressing the density n of the Cooper pairs in terms of the average distance r_a we can rewrite (2) as

$$r_a \equiv n^{-1/3} = \frac{1}{2}\left(\frac{\pi^2}{1.20257}\right)^{1/3} \frac{\hbar v_F}{k_B T_c} = 1.00856 \frac{\hbar v_F}{k_B T_c}. \tag{40}$$

This distance is of the order 10^{-4} cm for type-I superconductors. The ideal coherence length ξ_0 [11] measured far below T_c has the same order of magnitude.

Introduction of magnetic impurities in a sample is known [12,13] to make the critical temperature T_c smaller because the antiparallel spin configuration of the Cooper pairs are less favorable by the presence of magnetic impurities. If we assume that $\xi_0 = r_a$, the coherence length ξ_0 should become smaller *proportionately*. In this analysis, then $n^{1/3}$ dependence of T_c as well as its magnitude may be tested with experiments. Non-magnetic impurities can also reduce the number of Cooper pairs by breaking up the momentum pairing. but this effect is not as great as the same effect due to magnetic impurities. The number of Cooper pairs principally depends on the electron density, the band structure and the electron-phonon interaction. Thus, for very small concentrations of non-magnetic impurities, the critical temperature T_c should change little.

The B-E condensation approach similar to the present work can be extended to the layered high-T_c superconductors with the hypothesis [14] that electric currents flow only on the "copper" plane comprising Cu and O and perpendicular to the c-axis.

If free bosons move in 2D with the energy-momentum relation $\epsilon = cp = \frac{1}{2}v_F p$ and if the number of bosons is conserved, these bosons undergo a B-E condensation transition of the third order at the critical temperature T_c [6]

$$T_c = \hbar c(2\pi/1.645)^{1/2} n^{1/2} = 0.977\hbar v_F n^{1/2}. \tag{41}$$

The molar heat capacity C_V follows the T^2-law below T_c, reaches $4.38R$ at T_c, declines with a discontinuous slope at T_c and approaches the high-temperature-limit value 2 R. These exact results are not in violation of Hohenberg's theorem [15] that there can be no long range orders in 2D. This theorem was derived with the assumption of the sum rule representing the mass conservation [16]. Since bosons with $\epsilon = cp$ are massless, the theorem does not apply.

If we assume $r_a \equiv n^{-1/2} = \xi_0$, $\xi_0 = 14$ Å, $T_c = 94$ K for Y-Ba-Cu-O [17], the Fermi velocity v_F computed from (41) is 1.8×10^4 ms^{-1}, which is reasonable. The behăvior of the heat capacity C that (a) the C has no jump at T_c, and (b) it obeys the T^2 law just below T_c, is in good agreement with the extensive studies by Phillips *et al.* [18] for a number of high-T_c superconductors. We shall report a more complete theory in a separate publication [19].

APPENDIX: PROOF OF (15), (16), (20) AND (21)

Consider a 1D motion and omit the spin. The momentum eigenvalues $\{p_r\}$ are given by $p_r = 2\pi\hbar L^{-1} r$, where L is the periodicity length and r's are integers. In the bulk limit ($L \to \infty$, $N \to \infty$ while N/L–finite), the set (p_r) forms a continuous line extending over $(-\infty, \infty)$. The momentum distribution function $n(p)$ is defined through

$$n(p)\,dp\,L(2\pi\hbar)^{-1} = \begin{array}{l}\text{the relative probability of finding a fermion with a}\\ \text{momentum in } dp \text{ at } p.\end{array} \tag{A.1}$$

We wish to construct a quantum operator describing $n(p)$.

Let us introduce distributional (or coarse-grained) creation and annihilation operators defined by

$$c^\dagger(p)\Delta p^{1/2}\left(\frac{L}{2\pi\hbar}\right)^{1/2} = \sum_{p_j \subset \Delta p} \alpha_j^* c_j^\dagger, \quad c(p)\Delta p^{1/2}\left(\frac{L}{2\pi\hbar}\right)^{1/2} = \sum_{p_j \subset \Delta p} \alpha_j c_j, \tag{A.2}$$

where $c_j^\dagger$ and c_j are creation and annihilation operators satisfying the Fermi commutation relations (12), α_j phase factors of magnitude one, and the summation is taken over all of the momentum states p_j within the momentum interval Δp. Note that for a finite interval Δp the summation in the bulk limit must be taken over an infinite set. We now examine

$$c^\dagger(p)c(p)\Delta pL(2\pi\hbar)^{-1} = \hat{n}(p)\Delta pL(2\pi\hbar)^{-1}$$
$$= \sum_{p_j\subset\Delta p} c_j^\dagger c_j + \sum_{p_j}\sum_{p_\ell\subset\Delta p}{}' c_j^\dagger c_\ell \alpha_j^* \alpha_\ell \qquad (A.3)$$

where the prime on the double summation sign means the exclusion of equal indices $(j \neq k)$. Eqs. (A.1) and (A.3) indicate that the operator $\hat{n}(p) = c^\dagger(p)c(p)$ with the small interval limit $(\Delta p \to dp)$ taken can represent the distribution function $n(p)$ is the double sum does not contribute. This sum may be made to vanish by taking the following phase averaging.

The momentum eigenvalue p_r are obtained with the periodic boundary condition for the wave function $\phi(x)$

$$\phi(x + L) = \phi(x). \qquad (A.4)$$

Then, the field operator $\psi(x)$ which geneates the wave function $\phi(x)$ through $\langle 0|\psi(x) = \phi(x)$ has the same periodicity

$$\psi(x + L) = \psi(x). \qquad (A.5)$$

Let us choose the phase factor

$$\alpha_j = \exp(ip_j x/\hbar), \quad (x = \text{real parameter}) \qquad (A.6)$$

so as to be consistent with (A.4). In fact, from (A.2)

$$c(p)\Delta p^{1/2}\left(\frac{L}{2\pi\hbar}\right)^{1/2} = \sum_{p_j\subset\Delta p} e^{ixp_j/\hbar}c_j.$$

Summing these over the whole momentum range and multiplying the result by $(2\pi\hbar/L)^{1/2}$, we obtain

$$\left(\frac{2\pi\hbar}{L}\right)^{1/2}\sum_{p_j} e^{ixp_j/\hbar}c_j = \psi(x), \qquad (A.7)$$

which clearly satisfies the periodicity (A.5) desired. The sum may be equated with the field operator $\psi(x)$ by virtue of Dirac's transformation theory.

In the bulk limit, we may postulate that any observable physical property of a system under consideration be independent of the choice of the origin. In particular, we may require that the number density be constant. Equivalently, we may require that

$$\psi^\dagger(x)\psi(x) = \text{independent of } x. \qquad (A.8)$$

Substituting $\psi(x)$ and its Hermitean conjugate $\psi^\dagger(x)$ from (A.7) into (A.8) we obtain

$$\begin{aligned}\langle \alpha_j^* \alpha_\ell \rangle &\equiv \frac{1}{L}\int_0^L dx\, \alpha_j^*(x)\alpha_\ell(x) \\ &= \frac{1}{L}\int_0^L dx\, e^{ix(p_j - p_\ell)/\hbar} = 0 \quad \text{if } j \neq \ell. \end{aligned} \tag{A.9}$$

The eigenvalues of $c_j^\dagger c_j = n_j$ are 0 or 1. but because of the (infinite) sum in (A.3), the eigenvalues of $\hat{n}(p)$ are unlimited, that is, $0 \leq n'(p) < \infty$. In the bulk limit, the distributional operators $c^\dagger(p)$ and $c(p')$ defined in (A.2), satisfy the first of the Fermi commutation relations (16) containing Dirac's delta-function.

Let us now look at

$$c(p)^2 \Delta p = \frac{L}{4\pi\hbar} \sum_{p_j} \sum_{p_k \subset \Delta p} \alpha_j \alpha_k (c_j c_k + c_k c_j) = 0, \tag{A.10}$$

where (12) was used. This establishes a special case of the second equation in (16). The other cases can be worked out in a similar manner.

The theory and the results obtained here can be extended in a straightforward manner to the multi-dimensional motion, yielding (15) and (16) and also to the multi-particle space, yielding (20) and (21).

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