outside the integral. The latter then reduces to $4\pi l/3$ times the unit dyadic, and Eq. (28) becomes simply the local relation of Eq. (1).

The portion of the current which depends explicitly on the density, denoted by subscript D, is calculated in parallel fashion. Note that in the numerator of Eq. (18) we can write

$$\mathbf{k}\cdot\mathbf{v}-\omega=(\mathbf{k}\cdot\mathbf{v}-\omega-i\tau^{-1})+i\tau^{-1}, \tag{29}$$

where the quantity in parentheses cancels with the denominator and yields no current. Thus we find

$$\mathbf{J}_D=-\frac{ev_0}{4\pi l}\int d^3\xi\, e^{-\xi/l}\xi^{-3} \times\xi N(\mathbf{k},\omega)\exp[-i(\mathbf{k}\cdot\xi-\omega\xi/v_0)] \tag{30}$$

so that the Fourier inversion gives

$$\mathcal{J}_D(\mathbf{x},t)=-(ev_0/4\pi l)\int d^3\xi\, e^{-\xi/l}\xi^{-3}\xi n(\mathbf{x}',t'). \tag{31}$$

This is the diffusion current which must be added to Chambers' expression whenever longitudinal fields are acting in the metal. Here again it is of interest to check the static limit for fields which vary slowly in space. Then we have, approximately

$$n(\mathbf{x}',t')\approx n(\mathbf{x},t)-\xi\cdot\mathrm{grad}n(\mathbf{x},t). \tag{32}$$

The density gradient may now be taken outside the integral, so that the nonlocal, retarded diffusion formula of Eq. (31) reduces for this special case to Eq. (2), the simple uniform-gradient expression of kinetic theory.

To summarize, we began by emphasizing for the limiting case of time independence that it is necessary to include diffusion along with ohmic flow when describing longitudinal electric fields in metals. We then sketched a transport theory derivation of the relationship between the Fourier coefficients of the current and field. The result of this work is expressed by the conductivity functions of Eqs. (20) and (24). The diffusion is automatically included in the Boltzmann equation provided that the relaxation is based on the local density, rather than on the unperturbed density as is often done. Finally, we exhibited the explicit nonlocal, retarded relationship of current to field in the form of two integrals. The first is exactly Chambers' formula, while the second, given by Eq. (31), is the new diffusion term.

PHYSICAL REVIEW VOLUME 117, NUMBER 5 MARCH 1, 1960

Strong-Coupling Limit in the Theory of Superconductivity*

D. J. THOULESS†
Lawrence Radiation Laboratory, University of California, Berkeley, California
(Received June 22, 1959)

The Hamiltonian used by Bardeen, Cooper, and Schrieffer in their theory of superconductivity is studied in the strong-coupling limit. The complete set of energy levels can be found by using group theory, even for a finite system. An expression for the grand partition function can immediately be written down, and this expression can be evaluated in a simple manner for a large system. The results are in qualitative agreement with the weak-coupling theory, and in quantitative agreement with the strong-coupling limit of the expressions derived by Bardeen, Cooper, and Schrieffer. The second-order phase transition is a simple consequence of the form of the grand partition function. There is an energy gap independent of the total number of particles which goes to zero as the temperature approaches the critical temperature. The normal state is not metastable below the critical temperature.

1. INTRODUCTION

IN the theory of superconductivity developed by Bardeen, Cooper, and Schrieffer[1] (which we shall refer to as BCS) a system of interacting fermions with spin one-half is considered. The only interactions which are taken into account in the BCS theory are those between particles with opposite spin and momentum. Because of this, the single-particle states are paired off with each other. Each "pair state" consists of a single-particle state with a particular momentum and spin direction, together with the state of opposite momentum and spin. The interaction then carries a pair of particles from one pair state to another pair state. The kinetic energy is, of course, diagonal in the pair states, since it is diagonal in the single-particle states. If a pair state is singly occupied at any time, it remains singly occupied, since there is no other particle with which the one particle can interact, and since no pair of particles can scatter into an already occupied pair state.

This problem was studied in BCS by a variational method. It was shown by Bogoliubov, Zubarev, and Tserkovnikov[2] that the perturbation series for the part

* This work was performed under the auspices of the U. S. Atomic Energy Commission.
† Present address: Department of Mathematical Physics, Birmingham University, Birmingham, England.
[1] Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957).
[2] Bogoliubov, Zubarev, and Tserkovnikov, Doklady Akad. Nauk S.S.S.R. **117**, 788 (1957) [translation: Soviet Phys.-Doklady **2**, 535 (1957)].

of the free energy left out in the BCS solution vanishes term by term in the limit of an infinite (extended) system. This indicates that the BCS solution may be exact, but it is not a proof, as can be seen from the fact that there are many solutions which satisfy this criterion, although the free energy should be a unique function of temperature. In particular, the normal state satisfies this criterion at all temperatures, although the superconducting state, where it exists, has a lower free energy.

In the strong-coupling limit we take the interaction to be so strong (or else the effective mass to be so large) that the variation of the kinetic energy from particle to particle can be neglected, at least over a small region of momentum space. We suppose that there is a spherical shell within which the kinetic energy of each particle is a constant, ϵ, and the coupling between pair states is a constant, J. Outside this shell the particles have their normal kinetic energy but no interaction. We suppose that the Fermi surface is within the shell, so that the states on one side of the shell are fully occupied at low temperatures, whereas the states on the other side are completely empty.

The particles outside the shell and the particles in singly occupied pair states inside the shell behave like free fermions. The part of the Hamiltonian which affects the rest of the particles can be written as

$$H=\sum_{i=1}^{B} 2\epsilon b_i^\dagger b_i-\sum_{i=1}^{B}\sum_{j=1}^{B} J b_i^\dagger b_j, \tag{1}$$

where b_i annihilates and $b_i^\dagger$ creates a pair of particles in the pair state i. The sum runs over the B pair states in the shell which are not singly occupied. This problem has been solved exactly by Wada, Takano, and Fukuda,[3] who use the analogy between the operators b_i and spin operators, but a different method will be used here.

It can be seen that the form of Eq. (1) is unchanged if the labels of the B pair states are changed amongst themselves. For this reason, the eigenstates of the Hamiltonian must give rise to irreducible representations of the group of permutations of B objects, the "symmetric group." In Sec. 2 we find which these representations are, and what energy and degeneracy each one corresponds to; the eigenfunctions found form a complete set. In Sec. 3 we write down an exact expression for the grand partition function and evaluate it for a large system. The second-order phase transition appears in a very simple manner, and various other features of this model are compared with the BCS theory.

2. CONSTRUCTION OF THE EIGENFUNCTIONS

If we operate on the vacuum with D *different* operators $b_i^\dagger$, we construct a state with D pairs in the B pair states. Since the different operators commute, their order is immaterial, and we can construct $B!/D!(B-D)!$ mutually orthogonal wave functions in this way. These wave functions give all the ways of putting D pairs into B pair states. They are the basis of a reducible representation of the symmetric group, and the problem is to find the irreducible representations contained in it. We shall show that we can construct at least one wave function of a particular symmetry; then we know it is an eigenstate of a particular degeneracy and energy. We shall find that we can exhaust the $B!/D!(B-D)!$ available degrees of freedom in this way.

The irreducible representations of the symmetric group can be characterized by their Young diagram.[4] The Young diagrams which give us the desired representations have two rows, with $B-r$ squares in the first row and r squares in the second row. Now put the B operators $b_i^\dagger$ in order into the B squares, and add to this arrangement all the other arrangements which occur when we symmetrize within each row and then antisymmetrize within each column. We operate on the vacuum with the operators which occur in the first D squares of an arrangement, and add together the states we get from each arrangement. There is a factor -1 for each permutation within a column, and so we will get zero if $D<r$ or if $D>B-r$. If $r\leqslant D\leqslant B-r$, the coefficient of a component for which D of the first $B-r$ pair states are occupied is $D!(B-r-D)!r!$, and the coefficient of a component for which $D-1$ of the first $B-r$ pair states and one of the last r are occupied is $-(D-1)!(B-r-D+1)!r!$, and so on. We have now constructed wave functions with the appropriate symmetries, and it remains to find their energies and degeneracies.

The dimensionality of a representation, or the degeneracy of an eigenfunction, is equal to the character of the identity element of the group. This can be evaluated in the usual way,[5] and is found to be

$$l_r=\frac{B!(B-2r+1)}{r!(B-r+1)!}=\frac{B!}{r!(B-r)!}-\frac{B!}{(r-1)!(B-r+1)!}. \tag{2}$$

The sum of l_r from $r=0$ to $r=D$ or $B-D$, whichever is less, gives $B!/D!(B-D)!$ in either case, so we have found *all* the required eigenfunctions.

The character of a single permutation is found in the same way[5] to be

$$\chi_r=\frac{(B-2)!(B-2r+1)}{r!(B-r+1)!}(B^2-2rB-B+2r^2-2r). \tag{3}$$

The character χ_r is given by the expectation value of the operator P_{ij} which permutes the states i and j, summed over all l_r states of the irreducible representation. The expectation value of P_{ij} in one state, summed over all different combinations of i and j, is $B(B-1)\chi_r/2l_r$. The

[3] Wada, Takano, and Fukuda, Progr. Theoret. Phys. (Kyoto) **19**, 597 (1958).

[4] H. Boerner, *Darstellungen von Gruppen* (Springer-Verlag, Berlin, 1955), pp. 91–111.

[5] Reference 4, pp. 171–176.

probability that P_{ij} will permute two occupied states is $D(D-1)/B(B-1)$, the probability that it will permute two unoccupied states is $(B-D)(B-D-1)/B(B-1)$, and its expectation value in the case that it permutes an occupied and an unoccupied state is the expectation value of $b_i^\dagger b_j+b_j^\dagger b_i$. These can be added together to give

$$B(B-1)\chi_r/2l_r=\tfrac{1}{2}D(D-1)+\tfrac{1}{2}(B-D)(B-D-1)+\sum_i\sum_{j\neq i}\langle b_i^\dagger b_j\rangle. \quad (4)$$

Equations (2) and (3) can be substituted in this, and the result used to evaluate the expectation value of (1). This gives

$$\langle H\rangle=2\epsilon D-J[D(B-D+1)-r(B-r+1)]. \quad (5)$$

This result can also be derived by operating with H on the wave function for which an explicit construction has been given, and evaluating the coefficient of a particular component.

Since J is assumed to be positive (attractive interaction), and r is no greater than either D or $B-D$, Eq. (5) shows that the ground state has $r=0$, and the energy increases steadily with r. The spacing between the ground state and the first excited state is JB, and the spacing between successive levels decreases as r increases. Equation (2) shows that the ground state is nondegenerate, and the first excited state has degeneracy $\frac{1}{2}B(B-1)-1$. For $B=2D$, this agrees with BCS Eqs. (2.42) and (2.54) in the strong-coupling limit. Our B is equivalent to $2N(0)\hbar\omega$ in BCS. There are other excitations which can be made from the ground state. A pair can be broken up, and both particles left inside the shell, so that B is decreased by two and D is decreased by one; this raises the energy by $J(B-1)$. A particle can be excited from the Fermi sea into the shell, so that B is decreased by one; the energy is increased by JD plus the kinetic energy needed. All these and other processes need an energy of at least JB if the kinetic energy gap between the Fermi sea and the shell, and between the shell and the outside region of momentum space, is at least $\frac{1}{2}JB$.

We are chiefly interested in an extended system, and so we will suppose that B and D are proportional to the volume of the system, while J is inversely proportional to the volume. This means that the energy contributed to the ground state by the interaction is proportional to the volume, as the kinetic energy is, and the gap between the ground state and the first excited state is independent of the volume. The degeneracy of the rth excited state is proportional to the rth power of the volume. If r has its maximum value, the potential energy is zero or very close to zero, and the degeneracy is very great, so this state is closely related to the "normal" state.

3. STATISTICAL MECHANICS

Since we know all the energy levels of the system, we can write down an expression for the grand partition function. The particles inside the shell are independent of the particles outside the shell, and so we can treat the two subsystems separately. For the particles outside the shell, we have an ideal Fermi gas with a region of momentum space excluded, and so the statistical mechanics of this subsystem is straightforward. We therefore confine our attention to the particles inside the shell, whose behavior is determined by the Hamiltonian (1).

We suppose that there are K pair states inside the shell, but q of them are singly occupied, so that $B=K-q$. There are $K!/q!(K-q)!$ ways of choosing these q states, and 2^q ways of putting one particle into each of them. The energy of each single particle is ϵ, and the only restriction on q is that it should lie in the range zero to K. Using Eqs. (2) and (5), we write the grand partition function as

$$\begin{aligned}\mathfrak{Z}&=\mathrm{Tr}\exp[\beta(\mu N-H)]\\&=\sum_{q=0}^{K}\sum_{r=0}^{\frac{1}{2}(K-q)}\sum_{D=r}^{(K-q-r)}\frac{2^qK!(K-q-2r+1)}{q!r!(K-q-r+1)!}\\&\quad\times\exp\{\beta[(\mu-\epsilon)(q+2D)+JD(K-q-D+1)-Jr(K-q-r+1)]\}. \quad (6)\end{aligned}$$

The sum in (6) is over the three-dimensional space defined by the coordinates q, r, and D. The region over which the sum is taken is a tetrahedron bounded by the planes $q=0$, $r=0$, $D=r$, and $D+q+r=K$. The number of points in this tetrahedron is equal to its volume, which is $K^3/12$.

If we call the maximum value of the summand of Eq. (6) $\mathfrak{z}_0$, we know that $\mathfrak{z}_0<\mathfrak{z}<\mathfrak{z}_0K^3/12$. Quantities of physical interest are found by taking the logarithm of $\mathfrak{z}$ and dividing by the volume, so that $\mathfrak{z}_0$ is a very good approximation. The error goes as $3V^{-1}\log V$, where V is the volume of the system, although this is certainly an overestimate of the error. A local maximum of the summand is also interesting, since this will represent a metastable state of the system. We must look for maxima both in the interior of the tetrahedron and on its boundaries.

The summand increases rapidly as we go from the planes $q=0$ and $r=0$ into the interior of the tetrahedron, so we are interested in only the other two faces. As we go in a line parallel to the D axis from the faces $D=r$ and $D+q+r=K$, the summand increases by a factor of approximately $\exp[2\beta(\mu-\epsilon)+\beta J(K-q-2r)]$ and $\exp[-2\beta(\mu-\epsilon)+\beta J(K-q-2r)]$ in the two cases for a change in the value of D by one. This shows that a maximum can occur only on the face $D=r$ if $\mu<\epsilon$, and one can occur only on the face $D+q+r=K$ if $\mu>\epsilon$, since $K-q-2r$ is positive. The maximum value of the summand on either face occurs at

$$\begin{aligned}q&=\tfrac{1}{2}K\,\mathrm{sech}^2[\tfrac{1}{2}\beta(\mu-\epsilon)],\\r&=K[\exp(\beta|\mu-\epsilon|)+1]^{-2}. \quad (7)\end{aligned}$$

The condition for this to be a true maximum of the summand is that the summand should not increase towards the interior, and the condition $-2|\mu-\epsilon|+J(K-q-2r)<0$ implies

$$\beta<\beta_C=2|\mu-\epsilon|^{-1}\tanh^{-1}(2|\mu-\epsilon|/JK). \tag{8}$$

If we write down the condition for the summand to be a maximum at a point in the interior, we get the coupled equations

$$\begin{aligned} q&=2Ky(y+1)^{-2},\\ r&=K(y+1)^{-2},\\ D&=J^{-1}(\mu-\epsilon)+\tfrac{1}{2}(K-q), \end{aligned} \tag{9}$$

where

$$y=\exp[\tfrac{1}{2}\beta J(K-q-2r)]. \tag{10}$$

These equations can be combined to give the single equation for y,

$$\ln y=\tfrac{1}{2}\beta JK(y-1)(y+1)^{-1}, \tag{11}$$

which has the solution $y=1$, and also one solution greater than one if and only if $\beta JK>4$. The solution $y=1$ lies outside the tetrahedron unless $\mu=\epsilon$, and this case will be treated separately below. Equation (11) shows that the other solution for y is a monotone increasing function of β. The condition for the point (9) to lie inside the tetrahedron is

$$(y+1)^{-1}<\tfrac{1}{2}-J^{-1}K^{-1}|\mu-\epsilon|, \tag{12}$$

and this is equivalent to $\beta>\beta_C$, where β_C is the reciprocal of the *critical temperature* defined by Eq. (8). This shows that at all temperatures there is only one maximum of the summand, and this maximum lies in the interior of the tetrahedron for temperatures less than the critical temperature, but it lies on the face for temperatures greater than the critical temperature.

The case $\mu=\epsilon$ is particularly interesting, because it corresponds to the situation examined in BCS. The equation (8) for the critical temperature becomes

$$\beta_C=4/JK, \tag{13}$$

and there is a maximum of the summand in the interior below the critical temperature. There is also a stationary point in the middle of one edge, at $q=\frac{1}{2}K$, $r=K/4$, $D=K/4$, as can be seen from Eq. (7) or from Eq. (9) with $y=1$. As can be seen from Eq. (6), the factor $K-q-2r$ is important near this point, but its main effect is to shift the maximum of the summand by a distance proportional to $K^{\frac{1}{2}}$, so it will be ignored. As we go away from the edge, the summand increases by a factor $r(K-q-r)^{-1}\exp[\beta J(K-q-2r)]$ as r decreases by one. This factor is greater than unity in the interior of the tetrahedron below the critical temperature, and is less than unity above the critical temperature, so that this state is unstable below the critical temperature, and there is no metastable state.

In general, the summand of Eq. (6) falls off from its maximum value so rapidly that the quantities q, r, and D vary from the values given in Eqs. (7) and (9) by an amount proportional to $K^{\frac{1}{2}}$. Above the critical temperature, for $\mu\neq\epsilon$, the derivative of the summand in a direction normal to the face does not vanish, and so the quantities $D-r$ and $K-D-q-r$, for $\mu<\epsilon$ and $\mu>\epsilon$, respectively, fluctuate only by an amount independent of K. For $\mu=\epsilon$, the fluctuations of all three variables are proportional to $K^{\frac{1}{2}}$ even above the critical temperature. At the critical temperature, two stationary points of the summand coincide, and the second and third derivatives of the summand with respect to r also vanish. In this case, the fluctuations of r are proportional to $K^{\frac{1}{3}}$.

We can now substitute Eqs. (7) and (9) in (6) to get expressions for the thermodynamic functions. We shall refer to the state above the critical temperature as "normal" and to the state below the critical temperature as "superconducting," using the suffixes n and s to distinguish the thermodynamic functions for the two states. We find that the thermodynamic potential is

$$\begin{aligned} \Omega_n&=-\beta^{-1}\ln\mathfrak{z}\\ &=-2K\beta^{-1}\ln\{2\cosh[\tfrac{1}{2}\beta(\mu-\epsilon)]\}-K(\mu-\epsilon),\\ \Omega_s&=-2K\beta^{-1}\ln(y+1)+[2Ky/\beta(y+1)]\ln y\\ &\quad-\tfrac{1}{4}JK^2(y-1)^2(y+1)^{-2}\\ &\quad-K(\mu-\epsilon)-J^{-1}(\mu-\epsilon)^2. \end{aligned} \tag{14}$$

These functions must be equal at the critical temperature, since the points given by Eqs. (7) and (9) are the same. Differentiation with respect to the chemical potential gives the number of particles as

$$\begin{aligned} N_n&=K+K\tanh[\tfrac{1}{2}\beta(\mu-\epsilon)],\\ N_s&=K+2(\mu-\epsilon)/J, \end{aligned} \tag{15}$$

which is continuous at the critical temperature. The entropy can be obtained by differentiating Eq. (14) with respect to temperature and making use of Eq. (11), so that we have

$$\begin{aligned} S_n&=2Kk\ln\{2\cosh[\tfrac{1}{2}\beta(\mu-\epsilon)]\}\\ &\quad-Kk\beta(\mu-\epsilon)\tanh[\tfrac{1}{2}\beta(\mu-\epsilon)],\\ S_s&=2Kk\ln(y+1)-JK^2k\beta y(y-1)(y+1)^{-2}. \end{aligned} \tag{16}$$

The entropy also is continuous at the critical temperature; k is the Boltzmann constant.

It is clear that there is a second-order phase transition, since differentiation of Eq. (15) with respect to the chemical potential gives the isothermal compressibility as

$$\begin{aligned} \left(\frac{\partial V_n}{\partial p}\right)_{N,\beta}&=-\frac{V^2}{N^2}\left(\frac{\partial N}{\partial\mu}\right)_{V,\beta}\\ &=-\frac{V^2}{2N_n^2}\beta K\operatorname{sech}^2[\tfrac{1}{2}\beta(\mu-\epsilon)], \end{aligned} \tag{17}$$

$$\left(\frac{\partial V_s}{\partial p}\right)_{N,\beta}=-\frac{2V^2}{N_s^2J},$$

so that the superconducting state is more compressible than the normal state, unless $\mu=\epsilon$, when there is no discontinuity. There is also a discontinuity in the specific heat, which can be found by calculating the derivatives of Eqs. (15) and (16), since

$$C_n=T\left(\frac{\partial S}{\partial T}\right)_\mu-T\left(\frac{\partial N}{\partial T}\right)_\mu^2\Big/\left(\frac{\partial N}{\partial \mu}\right)_T=0, \tag{18}$$

$$C_s=2Kky[\ln y]^2/[(y+1)^2-\beta JKy].$$

The limiting value of C_s as y approaches unity is $3Kk$, so this quantity represents the discontinuity in specific heat for $\mu=\epsilon$. The phase transition occurs when the maximum of the summand of Eq. (6) goes from the interior of the tetrahedral region of summation to its surface.

Another quantity which must be calculated in order to compare our results with those of BCS is the variation of the energy gap with temperature. The energy gap is the energy needed to break up or excite one pair, and this can be calculated from Eqs. (5) and (9) as

$$2\epsilon_0=J(K-q-2r)=JK(y-1)/(y+1). \tag{19}$$

This decreases steadily up to the critical temperature with increasing temperature, but it goes to zero only if $\mu=\epsilon$. For $\mu=\epsilon$, we can compare many of our formulae with those of BCS taken in the strong-coupling limit. Equations (19) and (11) are equivalent to BCS Eq. (3.27); Eq. (13) agrees with BCS Eq. (3.28); and Eq. (16) agrees with BCS Eq. (3.34). The agreement of this model with the strong-coupling limit of BCS is therefore precise.

4. CONCLUSIONS

We have studied a simple model which can be solved exactly, and which gives a second-order phase transition. The eigenfunctions of the Hamiltonian were obtained by a group-theoretical method, and the thermodynamic functions were then calculated by straightforward algebra. This model is a strong-coupling limit of the BCS theory of superconductivity. The precise agreement with the BCS results is an interesting verification of the accuracy of those results. The qualitative features of the strong-coupling limit are very similar to those of the weak-coupling theory, and the main difference is that the excited states are discrete instead of forming a continuum of energy levels. Numerical values of important ratios are not changed much. For example, the ratio of the energy gap at zero temperature to kT_C is 4 in the strong-coupling limit and 3.50 in the weak-coupling limit, while the energy gap behaves like 6.9 $kT_C(1-T/T_C)^{\frac{1}{2}}$ instead of 6.4 $kT_C(1-T/T_C)^{\frac{1}{2}}$ near the critical temperature. Because of the simplicity of the model, it is possible to show that the normal state is not metastable in the absence of a magnetic field below the critical temperature.

5. ACKNOWLEDGMENT

I would like to thank Dr. B. R. Mottelson for his comments on this paper.