THERMODYNAMICS OF ANISOTROPIC SUPERCONDUCTORS

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We have solved the Bogolyubov equation for the energy gap in a superconductor for the anisotropic case. We show that in the weak coupling approximation a change in temperature leads to a change in the magnitude of the gap by a factor which is independent of the direction. The general behavior of the change in the thermodynamic quantities is qualitatively the same as in the isotropic case. The relative jump in the specific heat turns out to be larger than 1.4. An inequality of the same kind is also obtained for the critical magnetic field near the absolute zero.

THE theory of superconductivity was developed for an isotropic model.[1,2] The isotropic theory agrees qualitatively very well with experiment, but it does not agree completely quantitatively. From this theory it follows, for instance, that the relative jump in the specific heat $\Delta C/C_n$ at the transition point should be equal to 1.4 for all superconductors, while this quantity varies in practice from metal to metal. Furthermore, the isotropic theory gives for the low-temperature behavior of the relative critical field the relation

$$H_{cr}(T) / H_{cr}(0) = 1 - \chi (T / T_{cr})^2,$$

where $\chi = 1.06$. Experimentally, χ turns also out to be different for different superconductors.

The temperature dependence of the specific heat differs rather much from that predicted by theory. Moreover, experimental results[3,4] show that the energy gap possesses a well defined anisotropy in some superconductors. It is thus of interest to develop a theory for anisotropic superconductors.

Bogolyubov et al.[2] obtained for the energy gap $\Delta(\mathbf{p})$ at absolute zero an equation which is also suitable for the anisotropic case

$$\Delta (\mathbf{p}) = g \int U (\mathbf{p}, \mathbf{p}') \frac{\Delta (\mathbf{p}')}{\varepsilon (\mathbf{p}')} d^3p'. \tag{1}$$

Here g is the dimensionless coupling constant ($g \ll 1$), $U(\mathbf{p}, \mathbf{p}')$ the interaction potential of two pairs of electrons with momenta and spins in opposite directions, $\epsilon(\mathbf{p}) = \sqrt{\xi^2(\mathbf{p}) + \Delta^2(\mathbf{p})}$, where $\xi(\mathbf{p}) = \mathbf{v}_F(\mathbf{p} - \mathbf{p}_F)$, while $\mathbf{v}_F$ and $\mathbf{p}_F$ are the velocity and momentum on the Fermi surface.

The integration in (1) is performed in such a way that the values of $\xi' = \xi(\mathbf{p}')$ lie between $\pm\omega$ where ω is the Debye frequency. We are interested in values of $\mathbf{p}$ and $\mathbf{p}'$ such that $|\xi|$, $|\xi'| \lesssim \omega$. In that region $U(\mathbf{p}, \mathbf{p}')$, $\Delta(\mathbf{p})$, and $\Delta(\mathbf{p}')$ may be assumed to depend only on the directions $\mathbf{n} = \mathbf{p}/p$ and $\mathbf{n}' = \mathbf{p}'/p'$. Taking this into account and integrating over ξ in (1) we find

$$\Delta (\mathbf{n}) = g \int U (\mathbf{n}, \mathbf{n}') \Delta (\mathbf{n}') \ln \frac{2\omega}{\Delta (\mathbf{n}')} \frac{d\sigma'}{v_F'}, \tag{2}$$

where $d\sigma'$ is an elementary area on the Fermi surface.

Taking into account that g is small, we write the solution of Eq. (2) in the form

$$\Delta (\mathbf{n}) = 2\omega\varphi (\mathbf{n}) e^{-\Lambda/g}, \tag{3}$$

where $\varphi(\mathbf{n})$ is a dimensionless function, and Λ a constant quantity of the order of magnitude of unity. Substituting (3) into (2) we get in the first nonvanishing approximation for $\varphi(\mathbf{n})$ the equation

$$\varphi (\mathbf{n}) = \Lambda \int U(\mathbf{n}, \mathbf{n}') \varphi (\mathbf{n}') \frac{d\sigma'}{v_F'}. \tag{4}$$

Equation (4) is a homogeneous Fredholm type integral equation. One can easily symmetrize the kernel of Eq. (4). The quantity Λ is thus an eigenvalue of Eq. (4) and $\varphi(\mathbf{n})$ an eigenfunction of this equation.

We shall show that Λ is the lowest eigenvalue. Indeed, the energy of the superconducting groundstate E_s is a functional of $\Delta^2(\mathbf{n})$ and the energy of the normal state E_n is obtained from E_s by putting $\Delta(\mathbf{n}) = 0$. The difference $E_n - E_s$ is thus in first approximation a homogeneous quadratic functional of $\Delta^2(\mathbf{n})$ and is according to (3) proportional to $\exp(-2\Lambda/g)$. E_s will thus be a minimum when Λ is a minimum. We note that by virtue of a well-known theorem $\Delta(\mathbf{n})$ has no zeroes on the Fermi surface.

We denote by $\psi(\mathbf{n})$ the normalized solution of Eq. (4) which corresponds to the lowest eigenvalue. In that case $\varphi(\mathbf{n}) = Q\psi(\mathbf{n})$. To find the constant Q we must solve the next approximation. Putting $\varphi(\mathbf{n}) = Q\psi(\mathbf{n}) + \varphi_1(\mathbf{n})$ we get for $\varphi_1(\mathbf{n})$ the equation

$$\varphi_1(\mathbf{n}) = \Lambda \int U(\mathbf{n}, \mathbf{n}')\varphi_1(\mathbf{n}')\frac{d\sigma'}{v'_F} - gQ\int U(\mathbf{n}, \mathbf{n}')\psi(\mathbf{n}')\ln(Q\psi(\mathbf{n}'))\frac{d\sigma'}{v'_F}. \qquad (5)$$

This is an inhomogeneous Fredholm type equation and it is known that the corresponding homogeneous equation has a solution.

The condition that (5) have a solution gives, if one takes (4) into account, an equation for Q:

$$\int \psi^2(\mathbf{n})\ln(Q\psi(\mathbf{n}))\frac{d\sigma}{v_F} = 0. \qquad (6)$$

If we write the normalization condition for $\psi(\mathbf{n})$ in the form

$$\int \psi^2(\mathbf{n})\frac{d\sigma}{p_0 v_F} = 1, \qquad (7)$$

where p_0 is a quantity of the order of magnitude of the momentum on the Fermi surface, we get from (6)

$$Q = \exp\left\{-\int \psi^2(\mathbf{n})\ln\psi(\mathbf{n})\frac{d\sigma}{p_0 v_F}\right\}. \qquad (8)$$

We note that Eq. (8) and also the further calculations remain valid also when ω is assumed to be a function of the direction $\omega(\mathbf{n})$, so long as we substitute in (3) instead of ω a constant quantity $\tilde{\omega}$ such that

$$\ln\tilde{\omega} = \int \psi^2(\mathbf{n})\ln\omega(\mathbf{n})\frac{d\sigma}{p_0 v_F}. \qquad (9)$$

In the following we shall thus assume, without sacrificing generality, that ω is constant.

We now turn to the case of finite temperatures. In that case we must solve the equation

$$\Delta(\mathbf{p}) = g\int U(\mathbf{p}, \mathbf{p}')\frac{\Delta(\mathbf{p}')}{\varepsilon(\mathbf{p}')}[1 - 2f(\beta\varepsilon(\mathbf{p}'))]\,d^3p', \qquad (10)$$

where $f(x) = (e^x + 1)^{-1}$. As in the previous case, Eq. (9) leads to an integral equation on the Fermi surface:

$$\Delta(\mathbf{n}) = g\int U(\mathbf{n}, \mathbf{n}')\left[\ln\frac{2\omega}{\Delta(\mathbf{n}')} - F(\beta\Delta(\mathbf{n}'))\right]\frac{d\sigma'}{v'_F}, \qquad (11)$$

where

$$F(x) = \int_{-\infty}^{\infty} dy\,(y^2+1)^{-1/2} f(x\sqrt{y^2+1}). \qquad (12)$$

The function $F(x)$ was studied in great detail in the survey of Abrikosov and Khalatnikov.[5] As $x \to \infty$ it tends to zero as e^{-x}, and as $x \to 0$ it behaves asymptotically as

$$F(x) = -\ln(\gamma x/\pi) + \lambda x^2, \qquad (13)$$

where $\ln\gamma$ is Euler's constant and $\lambda = (7/8\pi^2)\zeta(3)$.

We look again for a solution of Eq. (11) in the form given by (3). In zeroth approximation we get again (4) so that $\varphi(\mathbf{n}) = Q\psi(\mathbf{n})$, as before, but Q is now a function of the temperature. We can thus make the following statement: when the temperature is changed the magnitude of the energy gap in different directions will change in the same ratio. This conclusion can, apparently, be verified experimentally. We get for the function $Q(T)$ the equation

$$\ln\frac{Q(T)}{Q(0)} + \int \psi^2(\mathbf{n})F(\beta Q(T)\psi(\mathbf{n}))\frac{d\sigma}{p_0 v_F} = 0. \qquad (14)$$

It is clear from Eq. (14) that $Q(T) < Q(0)$.

Equation (14) becomes unsuitable near the transition temperature where $Q(T)$ is small, because F diverges logarithmically. Using the asymptotic expression (13) for this case we get from (10)

$$\Delta(\mathbf{n}) = g\int U(\mathbf{n}, \mathbf{n}')\Delta(\mathbf{n}')\left[\ln 2\omega\beta\frac{\gamma}{\pi} - \lambda(\beta\Delta(\mathbf{n}'))^2\right]\frac{d\sigma'}{v'_F}, \qquad (15)$$

from which we get in zeroth approximation in $(T - T_{cr})/T_{cr}$ a solution in the same form as (3), while the transition temperature is determined by the equation

$$T_{cr} = (\gamma/\pi)\,2\omega e^{-\Lambda/g}. \qquad (16)$$

Near the transition point the equation for $Q(T)$ is of the form

$$Q^2 = A\frac{T_{cr} - T}{T_{cr}}, \qquad A = \left[\lambda\left(\frac{\pi}{\gamma}\right)^2\int \psi^4(\mathbf{n})\frac{d\sigma}{p_0 v_F}\right]^{-1}. \qquad (17)$$

Comparing the results obtained here with the solution of the equation for the gap in the isotropic case, we see that the picture of the behavior of the gap as a function of the temperature is not changed qualitatively.

We consider now how the anisotropy of the superconductor affects its specific heat $C_s(T)$. Using the well-known formula for the entropy

$$S(T) = -2\sum_{\mathbf{p}}\{f(\beta\varepsilon)\ln f(\beta\varepsilon) + [1 - f(\beta\varepsilon)]\ln(1 - f(\beta\varepsilon))\} \qquad (18)$$

and differentiating it with respect to the temperature, we get after some simple transformations the equation

$$C_s(T) = -\beta \frac{d}{d\beta} \frac{2}{(2\pi)^3} \int \Delta G(\beta\Delta) \frac{d\sigma}{v_F},$$

$$G(x) = 2x \int_0^\infty \operatorname{ch} 2\varphi \, f(x \operatorname{ch}\varphi) d\varphi. \qquad (19)^*$$

The asymptotic behavior of $G(x)$ was also given in reference 5:

$$G(x) = \pi^2/3x - x/2 + 7\zeta(3)\, x^3/16\pi^2, \qquad x \to 0,$$

$$G(x) = \sqrt{2\pi x}\, e^{-x}, \qquad x \to \infty. \qquad (20)$$

Near the transition point we get

$$C_s(T) = \frac{2T_{cr}}{(2\pi)^3} \int \frac{d\sigma}{v_F} \left(\frac{\pi^2}{3} + \frac{\pi^2 A}{2\gamma^2} \psi^2 \right), \qquad (21)$$

where A is defined by (17). The value of the specific heat of the normal phase C_n at the transition point is obtained from (21) by setting A equal to zero. We get thus for the jump in the specific heat

$$\Delta C/C_n(T_{cr}) = 3A/2\gamma^2. \qquad (22)$$

(We chose p_0 by putting $\int d\sigma/p_0 v_F = 1$.)

We compare now the value of A determined by (17) with the corresponding magnitude of A_{is} in the isotropic model

$$A_{is}/A = \int d\sigma \psi^4(\mathbf{n}) / p_0 v_F. \qquad (23)$$

From the normalization condition (7) follows that the integral on the right hand side of Eq. (23) is larger than unity as long as $\psi(\mathbf{n}) \neq$ const., and thus $A < A_{is}$. The isotropic model gives thus too large an estimate for the ratio $\Delta C/C_n(T_{cr})$.

We must now turn our attention to the discrepancy of this theoretical conclusion with experimental data[6-8] according to which for nearly all known cases $A > A_{is}$ (apart from Cd, Zn, and Tl). A possible cause of this discrepancy is that the interaction is in fact not a weak one and that there occurs experimentally a stronger singularity than a finite jump.†

We consider now the behavior of the specific heat at low temperatures. Using the asymptotic behavior of $G(x)$ as $x \to \infty$ we get from (19)

$$C_s(T) = \sigma \beta^{3/2} \Delta_{min}^{1/2} \exp\{-\beta \Delta_{min}(0)\}, \qquad (24)$$

where σ is a dimensionless constant of order of magnitude unity. We can use (3) and (16) to rewrite Eq. (24) as follows:

$$C_s(T) = \sigma \beta^{3/2} \sqrt{\Delta_{min}} \exp\{-Q(0)\psi_{min}\pi T_{cr}/\gamma T\}. \qquad (25)$$

From Eq. (8) the inequality $Q(0) < 1/\psi_{min}$ follows. The specific heat of an anisotropic superconductor is thus as function of the reduced temperature exponentially larger than the value which is predicted by the isotropic model. This result obtained already by Abrikosov and Khalatnikov[5] is well substantiated by experimental data.

In the intermediate temperature range the deviation of the specific heat from the curve obtained using the isotropic model must be large according to (19). Experimentally this deviation reaches, indeed, 30—40% (for instance,[7] for Zn and Al at $T \sim \frac{1}{2} T_{cr}$).

To find the critical magnetic field we use the appropriate expression from the Bardeen-Cooper-Schrieffer (BCS) theory [see, for instance, reference 5, Eq. (3.37)] but we must replace the quantity $\nu = p_0^2/\pi^2 v_F$ in the anisotropic case by an integral operator on the Fermi surface:

$$\frac{H_{cr}^2}{8\pi} = \frac{1}{2(2\pi)^3} \int \frac{d\sigma}{v_F} \Delta^2(\mathbf{n}) + \frac{T}{(2\pi)^3} \int \left[\Delta G(\beta\Delta) - \frac{\pi^2}{3} T \right] \frac{d\sigma}{v_F}. \qquad (26)$$

Using the solution of (3) for which we found for $\Delta(\mathbf{n})$ and the normalization (7) we get from (24)

$$\frac{H_{cr}^2}{8\pi} = \frac{1}{2(2\pi)^3} p_0 \left(\frac{\pi}{\gamma} T_{cr} \right)^2 Q^2(T) + \frac{T}{(2\pi)^3} \int \left[\Delta G(\beta\Delta) - \frac{\pi^2}{3} T \right] \frac{d\sigma}{v_F}. \qquad (27)$$

Near the absolute zero

$$\frac{H_{cr}^2}{8\pi} = \frac{1}{16\pi^3} p_0 \left(\frac{\pi}{\gamma} T_{cr} \right)^2 Q^2(0) - \frac{p_0 T^2}{24\pi} = \frac{H_{cr}^2(0)}{8\pi} \left(1 - 2\chi \frac{T^2}{T_{cr}^2} \right). \qquad (28)$$

$$\chi = \gamma^2/3Q(0). \qquad (29)$$

One sees easily from Eq. (8) that for any $\psi(\mathbf{n})$ different from unity $Q(0) < 1$ and we have thus from (29)

$$\chi > \chi_{is} = 1.06. \qquad (30)$$

The data on the measurements of the critical magnetic field which are given in Shoenberg's monograph[9] are in contradiction to this result (except Sn where $\chi = 1.07$). The fact that for such anisotropic superconductors as Zn and Al the quantity χ turns out to be very nearly equal to unity seems to be especially surprising. We must note that in fact there are no measurements in the low-temperature region and the values of χ mentioned a moment ago are extrapolations, the correctness of which can, apparently, not be assumed to be established. All the same, the reasons for the dis-

*ch = cosh.

†Note added in proof (February 8, 1961). According to an estimate by A. A. Abrikosov and L. P. Gor'kov (private communication) a deviation of the specific heat from its normal behavior (a finite jump) can only be manifest in a very narrow temperature range near the transition point, which is up to the present inaccessible experimentally.

crepancy between the theoretical conclusions and the experimental data are not clear to the present author. It is, apparently, necessary to elucidate first of all how an increase of the interaction constant g would influence the results. An analysis of this problem will be the subject of a subsequent communication.

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