d-wave pairing near the transition temperature*

N. D. Mermin
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850
(Received 1 October 1973)

The problem of minimizing the general fourth-order Ginzburg-Landau free energy for d-wave pairing in a homogeneous system is solved. The highly degenerate family of solutions arising when the fourth-order term has the elementary BCS form, is found to be associated with a point lying on the boundary of two regimes in the general parameter space. On either side of the boundary the degeneracy is reduced to the minimum required by gauge and rotational invariance, but in very different ways: on one side pairing is in a state with $L_z = 2$; on the other, pairing is in a state with $\langle \vec{L} \rangle = 0$. It is therefore essential to know the form of the corrections to the elementary BCS theory, whether or not they prove to be large.

I. INTRODUCTION

The newly discovered low-temperature phases of liquid ^{3}He have reawakened interest in theories of pairing with $L \neq 0$.[1] Within a pairing model there is conclusive evidence that the A phase is triplet pairing; whether the B phase is triplet or singlet pairing is presently less clear.[2] The question can be resolved by measurements of the magnetic susceptibility down to submillidegree temperatures, to determine whether its limiting low-temperature form is (singlet) or is not (triplet) zero. In the absence of conclusive measurements, models of the B phase with both odd and even L are being explored, with particular emphasis on p- or f-wave models for the triplet phase, and d-wave models for the singlet phase.

Earlier studies of pairing with $L \neq 0$ have been based on BCS theory in its most elementary form.[3] One of the more interesting aspects of the discoveries in ^{3}He has been that the elementary form of the BCS theory of triplet pairing does not describe the observed magnetic behavior of the A phase.[4] Spin fluctuations have been suggested as the mechanism underlying the failure of the elementary form of the theory.[5] It has also been pointed out that the observed behaviour of the susceptibility is contained within the general form of the Ginzburg-Landau free energy for p-wave pairing near T_c, provided the parameters that characterize the fourth-order term deviate enough from the values they assume in the elementary theory.[6] The spin-fluctuation model suggests that such deviations may indeed have the form and size required to account for what has been observed.[7]

In the case of d-wave pairing, it has been noted that the free energy of the elementary form of BCS theory gives a misleading description of the order parameter near T_c, even if deviations of the free energy from its elementary BCS form are not large.[6] This is because the elementary form of the d-wave free energy is minimized by a family of order parameters with a nontrivial degeneracy far in excess of that required by gauge and rotational invariance. From the point of view of a general free energy, however, this excess degeneracy is an accidental consequence of the particular values assumed by the elementary BCS forms for the parameters characterizing the fourth-order terms. The degeneracy is reduced to the minimum required by gauge and rotational invariance by slight deviations of the free energy from the elementary BCS form,[8] and it is with this far more restricted set of order parameters that one should build a description of d-wave pairing near T_c.

The purpose of this paper is to give, as a starting point for studies of d-wave pairing near T_c, the form of the energy gap that minimizes the general d-wave free energy. The general d-wave free energy and the special form it assumes in the elementary BCS model are described in Sec. II, and the solution is given for the problem of minimizing the general free energy. The derivation of the solution, though elementary, is not entirely trivial, and is summarized in the Appendix.

II. d-WAVE ORDER PARAMETER AND FREE ENERGY

It follows from the most elementary form of the BCS theory that just below T_c the d-wave order parameter Δ is determined by minimizing a free energy of the form

$$f_0 = \alpha_0 \langle |\Delta|^2 \rangle + \beta_0 \langle |\Delta|^4 \rangle \tag{1}$$

over all second degree spherical harmonics:

$$\Delta = \sum_{m=-2}^{2} a_m Y_{2m}. \tag{2}$$

Here $\alpha_0 \propto (T-T_c)$, $\beta_0>0$, and $\langle\cdots\rangle = \int d\Omega/4\pi$. By writing Δ in terms of a normalized Δ_0,

$$\Delta = \lambda\Delta_0, \quad \langle|\Delta_0|^2\rangle = 1, \tag{3}$$

and minimizing with respect to λ, the problem of minimizing f_0 can be expressed as the equivalent problem of minimizing

$$\hat{f}_0 = -(\alpha_0^2/4\beta_0)(\langle|\Delta_0|^4\rangle)^{-1}, \tag{4}$$

where

$$f_0^{\min} = \hat{f}_0^{\min}, \quad \Delta^{\min} = (-2f_0^{\min}/\alpha_0)^{1/2}\Delta_0^{\min}. \tag{5}$$

The form (1) of the free energy, however, is only a special case of the general fourth-order Ginzburg-Landau free energy for d-wave pairing,

$$f = \alpha\,\mathrm{Tr}B^*B + \beta_1|\mathrm{Tr}B^2|^2 + \beta_2(\mathrm{Tr}B^*B)^2 + \beta_3\,\mathrm{Tr}(B^2B^{*2}), \tag{6}$$

where Δ is here represented in the alternative form

$$\Delta = \sum_{\mu\nu} \hat{k}_\mu B_{\mu\nu}\hat{k}_\nu,$$

$$\hat{k} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta), \tag{7}$$

and B is a traceless symmetric tensor.

The general form (6) is arrived at by noting that the general fourth-order term must obey gauge and rotational invariance, and can therefore contain only contractions of productions containing two B's and two B^*'s. Since $\mathrm{Tr}B=0$, no B or B^* can be contracted with itself; as a result it is easily verified that there are just four distinct ways to form contractions when B is symmetric. Furthermore, the identity[9]

$$\mathrm{Tr}(B^*B)^2 = \tfrac{1}{2}|\mathrm{Tr}B^2|^2 + (\mathrm{Tr}B^*B)^2 - 2\,\mathrm{Tr}(B^{*2}B^2), \tag{8}$$

which holds for any traceless 3×3 matrix B, reduces the number of independent fourth-order terms to three. That three independent parameters are required follows from the form of the solution to the general minimization problem given below, in which three different matrices B will be specified leading to three linearly independent combinations of β_1, β_2, and β_3, when substituted into the fourth-order terms in the general free energy (6).

It is also convenient to write the general minimization problem in terms of a normalized order parameter:

$$\hat{f} = -(\tfrac{1}{4}\alpha^2)(\beta_1|\mathrm{Tr}B_0^2|^2 + \beta_2 + \beta_3\,\mathrm{Tr}\,B_0^{*2}B_0^2)^{-1}, \tag{9}$$

where

$$\mathrm{Tr}B_0^*B_0 = 1, \tag{10}$$

and

$$f^{\min} = \hat{f}^{\min}, \quad B^{\min} = (-2f^{\min}/\alpha)^{1/2}B_0^{\min}. \tag{11}$$

By inserting the order parameter (7) into the special BCS form (1) of the free energy, performing the angular averages, and exploiting the identity (8), one establishes that the elementary form (1) of the free energy is a special case of the general form (6) assumed when

$$\alpha = \tfrac{2}{15}\alpha_0, \quad \beta_2 = 2\beta_1 = \tfrac{8}{315}\beta_0, \quad \beta_3 = 0. \tag{12}$$

Substituting these values of the parameters into (9), we find that

$$\hat{f}_0 = -(\alpha_0^2/4\beta_0)\tfrac{7}{10}(1 + \tfrac{1}{2}|\mathrm{Tr}B_0^2|^2)^{-1}, \tag{13}$$

which is evidently minimized by any B_0 with $\mathrm{Tr}(B_0)^2 = 0$. Thus the elementary BCS form of the free energy assumes its minimum value,[10]

$$f_0^{\min} = -\tfrac{7}{10}(\alpha_0^2/4\beta_0), \tag{14}$$

for any order parameter satisfying

$$\langle\Delta^2\rangle \propto \mathrm{Tr}B_0^2 = 0, \tag{15}$$

i.e., for any order parameter in which the coefficient of Y_{20} in the expansion (2) is given by

$$a_0^2 = -2(a_1a_{-1} + a_2a_{-2}), \tag{16}$$

regardless of the values of a_1, a_{-1}, a_2, or a_{-2}.

From the perspective of the general form (9), this vast degeneracy is an accidental consequence of the vanishing of β_3. In the general case, for given β_2, the portion of the $\beta_1-\beta_3$ plane consistent with the general requirement of thermodynamic stability, divides into three subregions (Fig. 1). In two regions (I and II) the solution is unique (to within a constant phase factor and a rotation). The elementary BCS case lies on the boundaries of these regions. In the third region (III) there is still some excess degeneracy, though not as much as in the elementary BCS case. The regions and solutions are as follows[11]

Region of stability. Stability requires a positive definite fourth-order term. This in turn requires a positive β_2, and restricts the $\beta_1-\beta_3$ plane to the region (see Fig. 1):

$$\beta_3 > -3\beta_2, \quad 2\beta_1 + \beta_3 > -2\beta_2. \tag{17}$$

Region I. $\beta_3 > -\beta_1 + |\beta_1|$. Here the minimum is given by

$$\Delta \propto (\hat{k}_x + i\hat{k}_y)^2 \propto Y_{22}. \tag{18}$$

Except for a constant phase factor and a rotation, the solution is unique. At the minimum

$$f^{\min} = -\alpha^2/4\beta_2. \tag{19}$$

Region II. $0 > \beta_3 > -6\beta_1$. Here the minimum is given by

$$\Delta \propto \hat{k}_x^2 + e^{2\pi i/3}\hat{k}_y^2 + e^{4\pi i/3}\hat{k}_z^2. \tag{20}$$

Except for a constant phase factor and a rotation, the solution is again unique. At the minimum

$$f^{\min} = -\alpha^2/4(\beta_2 + \tfrac{1}{3}\beta_3). \tag{21}$$

Region III. $\beta_3 < -4\beta_1 - 2|\beta_1|$. Here the minimum is given by *any* Δ_0 that is real (except for a constant phase factor). At the minimum

$$f^{\min} = -\alpha^2/4(\beta_1 + \beta_2 + \tfrac{1}{2}\beta_3). \tag{22}$$

Within regions I and II the best order parameters lie within the family (16) of minima of the elementary BCS free energy, the elementary BCS case (12) lying on the I-II boundary (see Fig. 1). A reliable computation of β_1 and β_3 has yet to be done, but assuming they do not deviate so much from the form (12) as to be in region III, one should base studies of d-wave pairing near T_c on order parameters of the form (18) or (20), but not of any of the other inequivalent forms consistent with (16).

Note that the solution in region I has maximally aligned orbital angular momentum, while that in region II (and III) has a vanishing expectation value of $\vec{L}$ along any axis. Thus even if corrections to the elementary BCS case should prove small, they will determine some very fundamental properties of the ordered state.

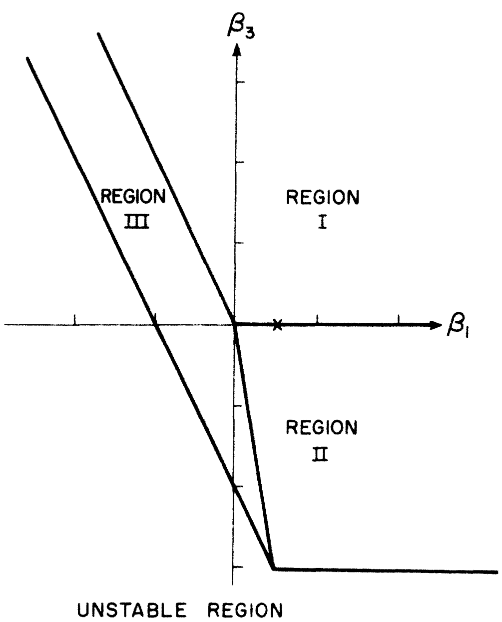

FIG. 1. Parameter space for the general fourth-order d-wave free energy. The scale on the β_1 and β_3 axes is in units of β_2, which stability requires to be positive. The point $\beta_1 = \frac{1}{2}\beta_2$, $\beta_3 = 0$, corresponding to the elementary BCS case, is indicated by an "x." In regions I and II the equilibrium order parameters are unique (to within a constant phase factor and a rotation) and are given by $\Delta \propto (\hat{k}_x + i\hat{k}_y)^2$ (region I) and $\Delta \propto \hat{k}_x^2 + e^{2\pi i/3}\hat{k}_y^2 + e^{4\pi i/3}\hat{k}_z^2$ (region II). In region III the free energy is minimized by any suitably normalized order parameter that is real (to within a constant phase factor).

APPENDIX

The following theorem provides the key to solving the d-wave problem near T_c: Any 3×3 matrix M with zero trace obeys the identity

$$\phi(M) = \mathrm{Tr}M^4 - \tfrac{1}{2}(\mathrm{Tr}M^2)^2 = 0. \tag{23}$$

To prove the theorem, note that if M is Hermitian with eigenvalues m_1, m_2, and $-(m_1+m_2)$, then (23) reduces to the trivial identity

$$m_1^4 + m_2^4 + (m_1+m_2)^4 - \tfrac{1}{2}[m_1^2 + m_2^2 + (m_1+m_2)^2]^2 = 0. \tag{24}$$

For general traceless M, define the traceless matrix

$$N(\lambda) = \tfrac{1}{2}(1 - i\lambda)M + \tfrac{1}{2}(1 + i\lambda)M^\dagger, \tag{25}$$

which is Hermitian for any real λ, so that $\phi[N(\lambda)] = 0$. But $\phi[N(\lambda)]$ is a fourth-degree polynomial in λ, and must therefore vanish for all λ if it vanishes for all real λ. Since $N(i) = M$, this establishes (23).

As a corollary of (23), if $M = X + \mu Y$, with $\mathrm{Tr}(X) = \mathrm{Tr}(Y) = 0$, then the coefficient of each power of μ in $\phi(M)$ must vanish. Looking, in particular, at the coefficient of μ^2, we find

$$0 = 4\,\mathrm{Tr}X^2Y^2 + 2\,\mathrm{Tr}(XY)^2 - 2(\mathrm{Tr}XY)^2 - \mathrm{Tr}X^2\,\mathrm{Tr}Y^2. \tag{26}$$

This identity reduces to (8) above, in the case $X = B$, $Y = B^*$, and is of further use in the analysis below.

According to (9), to minimize the free energy we must minimize

$$g(B_0) = \beta_1|\mathrm{Tr}B_0^2|^2 + \beta_2 + \beta_3\,\mathrm{Tr}B_0^{*2}B_0^2, \tag{27}$$

subject to the normalization condition $\mathrm{Tr}(B_0^*B_0) = 1$ [Eq. (10)]. Since $g(B_0)$ is independent of a multiplicative phase factor in B_0, it suffices to consider only B_0 satisfying

$$\mathrm{Re}(\mathrm{Tr}B_0^2) = 0. \tag{28}$$

Letting

$$\mathrm{Re}B_0 = X, \quad \mathrm{Im}B_0 = Y, \tag{29}$$

condition (28) and the normalization condition (10) require

$$\mathrm{Tr}X^2 = \mathrm{Tr}Y^2 = \tfrac{1}{2}. \tag{30}$$

Since X and Y are traceless, they also obey (23), and therefore

$$\mathrm{Tr}X^4 = \mathrm{Tr}Y^4 = \tfrac{1}{8}. \tag{31}$$

Using the identities (26), (30), and (31), we can reduce (27) to

$$g(B_0)=\beta_2+\tfrac{1}{2}\beta_3+(4\beta_1+2\beta_3)(\mathrm{Tr}XY)^2-4\beta_3\,\mathrm{Tr}X^2Y^2. \tag{32}$$

To minimize $g(B_0)$ in the form (32), we work in the representation in which the real symmetric matrix X is diagonal, with eigenvalues x_1, x_2, and x_3. It is easily verified that a general parametrization for three real numbers satisfying

$$x_1+x_2+x_3=0, \quad x_1^2+x_2^2+x_3^2=\tfrac{1}{2}, \tag{33}$$

is

$$x_n=\sqrt{\tfrac{1}{3}}\,\sin(\theta+\tfrac{2}{3}n\pi), \quad n=1,2,3. \tag{34}$$

The further conditions

$$\mathrm{Tr}Y=0, \quad \mathrm{Tr}Y^2=\tfrac{1}{2}, \tag{35}$$

can be insured by a parametrization similar to (34) for the diagonal elements of Y,[12]

$$Y_{nn}=(\tfrac{1}{3}c)^{1/2}\sin(\theta+\varphi+\tfrac{2}{3}n\pi), \quad n=1,2,3, \tag{36}$$

and the parametrization

$$\begin{aligned} Y_{12}&=\tfrac{1}{2}(1-c)^{1/2}z_3,\\ Y_{23}&=\tfrac{1}{2}(1-c)^{1/2}z_1,\\ Y_{31}&=\tfrac{1}{2}(1-c)^{1/2}z_2, \end{aligned} \tag{37}$$

for the off-diagonal elements. Here

$$0\leq c\leq 1 \tag{38}$$

and

$$z_1^2+z_2^2+z_3^2=1. \tag{39}$$

Substituting the forms (34), (36), and (37) into the form (32) for $g(B_0)$, one finds

$$g(B_0)=cg_1(B_0)+(1-c)g_2(B_0), \tag{40}$$

where

$$g_1(B_0)=\beta_2+\tfrac{1}{3}\beta_3+(\beta_1+\tfrac{1}{6}\beta_3)\cos^2\varphi, \tag{41}$$

$$\begin{aligned} g_2(B_0)=\beta_2&+\tfrac{1}{6}\beta_3\\ &-\tfrac{1}{6}\beta_3[\tfrac{3}{2}(\textstyle\sum z_n^4)-\tfrac{1}{2}]^{1/2}\cos(2\theta+\delta), \end{aligned} \tag{42}$$

and

$$\tan\delta=\sqrt{3}\,(z_1^2-z_2^2)/(2z_3^2-z_1^2-z_2^2). \tag{43}$$

Since $g_1(B_0)$ depends only on φ, and $g_2(B_0)$ depends only on θ and the z_n, they can be minimized independently, and c should be taken to be 1 or 0, according to whether g_1 or g_2 is the lower. Thus

$$f^{\min}=-\alpha^2/4g^{\min}=-\alpha^2/4\min(g_1^{\min},g_2^{\min}). \tag{44}$$

The separate $g_i(B_0)$ can be minimized by inspection[13]:

$$g_1^{\min}=\beta_2+\tfrac{1}{3}\beta_3, \quad \cos\varphi=0, \quad \text{if } \beta_1+\tfrac{1}{6}\beta_3>0; \tag{45}$$

$$g_1^{\min}=\beta_1+\beta_2+\tfrac{1}{2}\beta_3, \quad \cos^2\varphi=1, \quad \text{if } \beta_1+\tfrac{1}{6}\beta_3<0; \tag{46}$$

$$g_2^{\min}=\beta_2, \quad \cos2\theta=1, \quad z_1=z_2=0, \quad \text{if } \beta_3>0; \tag{47}$$

$$g_2^{\min}=\beta_2+\tfrac{1}{3}\beta_3, \quad \cos2\theta=-1, \quad z_1=z_2=0, \quad \text{if } \beta_3<0. \tag{48}$$

The stability condition (17) is just the requirement that all four possibilities give a positive g at the minimum (and hence a positive fourth-order term in the original free energy). A straightforward examination of (45)–(48) reveals that the absolute minima of $g(B_0)$ are indeed as described in Sec. II, the minimum being given by (47) in region I, (45) or (48) in region II,[14] and (46) in region III.

---

*Work supported in part by the National Science Foundation under Grant No. GH-36457 and also under Grant No. GH-33637 through the Cornell Materials Science Center, Report No. 2099.

[1]D. D. Osheroff, W. J. Gully, R. C. Richardson, and D. M. Lee, Phys. Rev. Lett. 29, 920 (1972). At the time of this writing the most recent experimental study is by D. N. Paulson, R. T. Johnson, and J. C. Wheatley, Phys. Rev. Lett. 31, 746 (1973), where references to many of the other experiments may be found.

[2]The evidence for triplet pairing in the A phase is reviewed by N. D. Mermin and V. Ambegaokar, in *Nobel Symposia—Medicine and Natural Sciences* (Academic, New York, to be published), Vol. 24. The most recent data on the susceptibility in the B phase (D. N. Paulson *et al.*, Ref. 1) is still inconclusive.

[3]See, for example, V. Ambegaokar and N. D. Mermin, Phys. Rev. Lett. 30, 81 (1973), and references cited therein.

[4]This was first emphasized by A. J. Leggett, Phys. Rev. Lett. 29, 1227 (1972).

[5]P. W. Anderson and W. F. Brinkman, Phys. Rev. Lett. 30, 1108 (1973).

[6]N. D. Mermin and G. Stare, Phys. Rev. Lett. 30, 1135 (1973).

[7]P. W. Anderson and W. F. Brinkman (to be published).

[8]If the deviations are not slight a regime may be reached (Region III below) in which excess degeneracy (of a different kind) is present.

[9]The proof of this identity (which is the essential step in minimizing the free energy in the elementary BCS case) is given in the Appendix. See Eq. (26) and the sentence that follows.

[10]As far as I know this result was first derived over ten years ago by V. J. Emery (private communication). A derivation has recently been given by G. Barton and

M. A. Moore (unpublished). The simplicity of the derivation given here is (in my opinion) startling. The form of the simple BCS d-wave order parameter at general temperatures has been examined by P. W. Anderson and P. Morel, Phys. Rev. 123, 1911 (1961).

[11] The results that follow are derived in the Appendix.

[12] Since $g(B_0)$ [Eq. (32)] does not depend on the sign of any of the Y_{mn}, the apparently distinct [given Eq. (34)] parametrization, $Y_{nn} = \sin(\theta + \varphi - \frac{2}{3}n\pi)$, need not be considered [for the change of variables $\varphi \to -\varphi - 2\theta$ reduces it back to the form (36), except for an over-all change in sign].

[13] In the case of g_2, if z_1 or z_2 is taken as the nonvanishing z_n, the change in the phase δ [Eq. (43)] results in a change in θ, which simply produces the corresponding shift in the x_n.

[14] The minimum (48) is, like the minimum (45), of the type (20) appropriate to region II, but in the case (48) the axes in (20) are not the principle axes of the matrix X.