

A Few Important Results from the BCS Paper ^① Phys. Rev. 108, 1175 (1957)

Minimization of the Free Energy

If the expressions (3.13) and (3.14) are introduced into (3.9) and (3.12), the free energy becomes

$$F = 2 \sum_{\mathbf{k}} |\epsilon_{\mathbf{k}}| [f_{\mathbf{k}} + (1 - 2f_{\mathbf{k}})h_{\mathbf{k}}(|\epsilon_{\mathbf{k}}|)] - \sum_{\mathbf{k}, \mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} [h_{\mathbf{k}}(1 - h_{\mathbf{k}})h_{\mathbf{k}'}(1 - h_{\mathbf{k}'})]^{\frac{1}{2}} \times \{(1 - 2f_{\mathbf{k}})(1 - 2f_{\mathbf{k}'})\} - TS. \quad (3.16)$$

When we minimize F with respect to $h_{\mathbf{k}}$, we find that

$$2\epsilon_{\mathbf{k}} - \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} [h_{\mathbf{k}'}(1 - h_{\mathbf{k}'})]^{\frac{1}{2}} (1 - 2f_{\mathbf{k}'}) \times \frac{(1 - 2h_{\mathbf{k}})}{[h_{\mathbf{k}}(1 - h_{\mathbf{k}})]^{\frac{1}{2}}} = 0, \quad (3.17)$$

or

$$\frac{[h_{\mathbf{k}}(1 - h_{\mathbf{k}})]^{\frac{1}{2}}}{1 - 2h_{\mathbf{k}}} = \sum_{\mathbf{k}'} \frac{V_{\mathbf{k}\mathbf{k}'} [h_{\mathbf{k}'}(1 - h_{\mathbf{k}'})]^{\frac{1}{2}} (1 - 2f_{\mathbf{k}'})}{2\epsilon_{\mathbf{k}}}, \quad (3.18)$$

where the energy $\epsilon_{\mathbf{k}}$ is measured relative to the Fermi energy and $\epsilon_{\mathbf{k}} < 0$ for $k < k_F$. Assuming as before that the interaction can be replaced by a constant average matrix element $-V$, defined by (2.34) for $|\epsilon_{\mathbf{k}}| < \hbar\omega$ and by zero outside this region, it follows that $h_{\mathbf{k}}$ is again of the form

$$h_{\mathbf{k}} = \frac{1}{2} [1 - (\epsilon_{\mathbf{k}}/E_{\mathbf{k}})], \quad (3.19)$$

and

$$[h_{\mathbf{k}}(1 - h_{\mathbf{k}})]^{\frac{1}{2}} = \frac{1}{2} \epsilon_0 / E_{\mathbf{k}}. \quad (3.20)$$

The energy $E_{\mathbf{k}}$, a positive definite quantity, is defined as

$$E_{\mathbf{k}} = +(\epsilon_{\mathbf{k}}^2 + \epsilon_0^2)^{\frac{1}{2}}, \quad (3.21)$$

where

$$\epsilon_0 = V \sum_{\mathbf{k}'} [h_{\mathbf{k}'}(1 - h_{\mathbf{k}'})]^{\frac{1}{2}} (1 - 2f_{\mathbf{k}'}). \quad (3.22)$$

It will turn out that $2\epsilon_0$ is the magnitude of the energy gap in the single-particle density of states and therefore the distribution of ground pairs is determined by the magnitude of the gap at that temperature.

Their notation

$$\Psi = \prod_{\mathbf{k}} \left[\underbrace{(1 - h_{\mathbf{k}})^{\frac{1}{2}}}_{u_{\mathbf{k}}} + \underbrace{h_{\mathbf{k}}^{\frac{1}{2}} b_{\mathbf{k}}^{\dagger}}_{v_{\mathbf{k}}} \right] \Phi_0$$

so

Free energy from excited quasiparticles and interactions between them.

One form of the gap equation

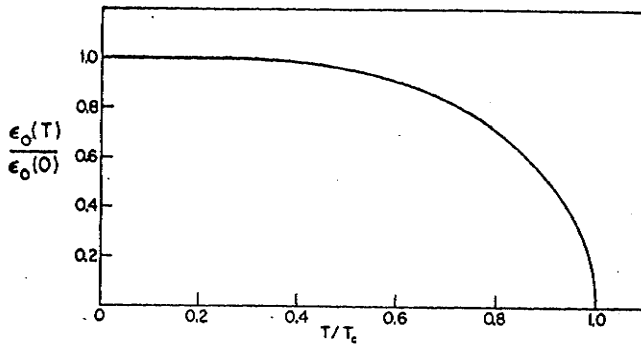


FIG. 1. Ratio of the energy gap for single-particle-like excitations to the gap at $T=0^\circ\text{K}$ vs temperature.

(3.22) becomes (dividing by ϵ_0)

$$\frac{1}{N(0)V} = \int_0^{\hbar\omega} \frac{d\epsilon}{(\epsilon^2 + \epsilon_0^2)^{3/2}} \tanh\left[\frac{1}{2}\beta(\epsilon^2 + \epsilon_0^2)^{1/2}\right], \quad (3.27)$$

where we have replaced the sum by an integral and used the fact that the distribution functions are symmetric in holes and electrons with respect to the Fermi energy. The transition temperature, T_c , is defined as the boundary of the region beyond which there is no real, positive ϵ_0 which satisfies (3.27). Above T_c therefore, $\epsilon_0=0$ and $f(E_k)$ becomes $f(\epsilon_k)$, so that the metal returns to the normal state. Below T_c the solution of (3.27), $\epsilon_0 \neq 0$, minimizes the free energy and we have the superconducting phase. Thus (3.26) can be used to determine the critical temperature and we find

$$\frac{1}{N(0)V} = \int_0^{\hbar\omega} \frac{d\epsilon}{\epsilon} \tanh\left(\frac{1}{2}\beta\epsilon\right), \quad (3.28)$$

or

$$kT_c = 1.14\hbar\omega \exp\left[-\frac{1}{N(0)V}\right], \quad (3.29)$$

as long as $kT_c \ll \hbar\omega$, which corresponds to the weak-coupling case discussed in Sec. II. The transition temperature is proportional to $\hbar\omega$, which is consistent with the isotope effect. The small magnitude of T_c compared to the Debye temperature is presumably due to the cancellation of the phonon interaction and the screened Coulomb interaction for transitions of importance in describing the superconducting state, and the resulting effect of the exponential.

← Temperature dependence of the gap: $\epsilon_0 \equiv \Delta_0$
notation.
modern

A plot of the energy gap as a function of temperature is given in Fig. 1. The ratio of the energy gap at $T=0^\circ\text{K}$ to kT_c is given by combining (2.36) and (3.28):

$$2\epsilon_0/kT_c = 3.50. \quad (3.30)$$

From the law of corresponding states, this ratio is predicted to be the same for all superconductors. Near

T_c , the gap may be expressed as

$$\epsilon_0 = 3.2kT_c[1 - (T/T_c)]^{1/2}, \quad (3.31)$$

which has the form suggested by Buckingham.⁸³

← Famous BCS equation

$$k_B T_c = 1.14 \hbar \omega e^{-1/2}$$

$$\frac{H_c^2}{8\pi} = N(0)(\hbar\omega)^2 \left\{ \left[1 + \left(\frac{\epsilon_0}{\hbar\omega} \right)^2 \right]^{\frac{1}{2}} - 1 \right\} - \frac{\pi^2}{3} N(0)(kT)^2$$

$$\times \left\{ 1 - \beta^2 \int_0^\infty d\epsilon \left[\frac{2\epsilon^2 + \epsilon_0^2}{E} \right] f(\beta E) \right\}. \quad (3.38)$$

← Critical field $H_c(T)$.

A plot of the critical field as a function of $(T/T_c)^2$ is given in Fig. 2. The curve agrees fairly well with the $1 - (T/T_c)^2$ law of the Gorter-Casimir two-fluid model,¹⁹ the maximum deviation being about four percent. There is good experimental support for a similar deviation in vanadium, thallium, indium, and tin; however, our deviation appears to be somewhat too large to fit the experimental results.

The critical field at $T=0$ is

$$H_0 = [4\pi N(0)]^{\frac{1}{2}} \epsilon_0(0) = 1.75 [4\pi N(0)]^{\frac{1}{2}} kT_c, \quad (3.39)$$

where $2\epsilon_0(0)$ is the energy gap at $T=0$ and the density of Bloch states $N(0)$ is taken for a system of unit volume.

A law of corresponding states follows from (3.39) and may be expressed as

$$\gamma T_c^2 / H_0^2 = \frac{1}{6} \pi [kT_c / \epsilon_0(0)]^2 = 0.170, \quad (3.40)$$

where the electronic specific heat in the normal state is given by

$$C_{en} = \gamma T \text{ (ergs/}^\circ\text{C cm}^3\text{)}, \quad (3.41)$$

and

$$\gamma = \frac{2}{3} \pi^2 N(0) k^2. \quad (3.42)$$

The Gorter-Casimir model gives the value of 0.159 for the ratio (3.40). The scatter of experimental data is too great to choose one value over the other at the present time.

Near $T=0$, the gap is practically independent of temperature and large compared to kT , and hence for

$T/T_c \ll 1$ we have the relation

$$H_c^2 = H_0^2 [1 - \frac{2}{3} \pi^2 (kT/\epsilon_0)^2], \quad (3.43)$$

or

$$H_c \cong H_0 [1 - 1.07 (T/T_c)^2]. \quad (3.44)$$

This approximation corresponds to neglecting the free-energy change of the superconducting state, the total effect coming from F_n .

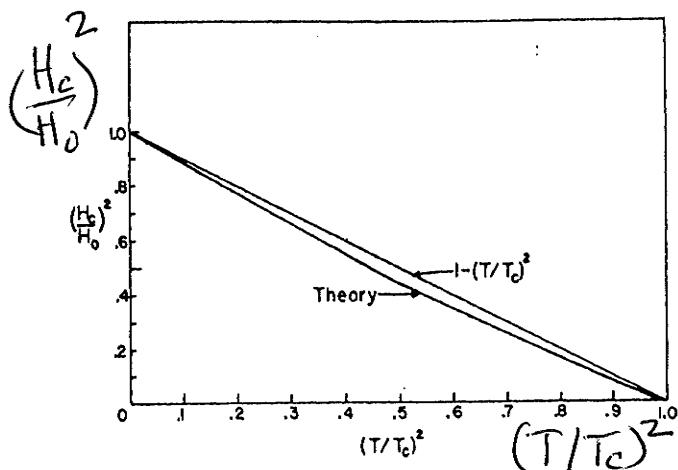


FIG. 2. Ratio of the critical field to its value at $T=0^\circ\text{K}$ vs $(T/T_c)^2$. The upper curve is the $1 - (T/T_c)^2$ law of the Gorter-Casimir theory and the lower curve is the law predicted by the theory in the weak-coupling limit. Experimental values generally lie between the two curves.

Heat Capacity Jump at T_c .
Also, low T limit.

numerical
solution

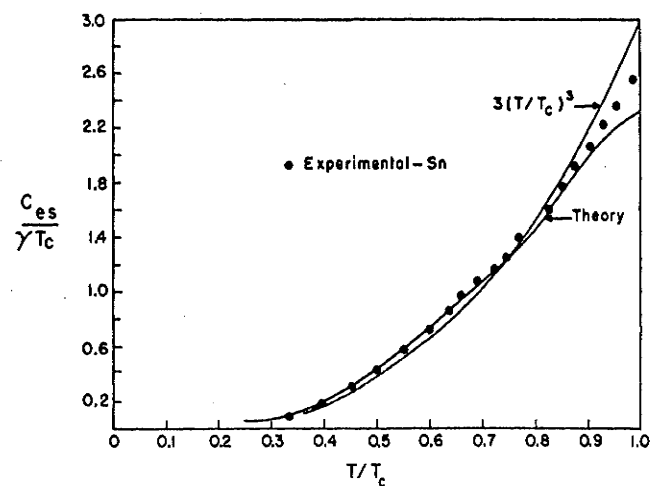
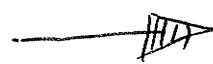


FIG. 3. Ratio of the electronic specific heat to its value in the normal state at T_c vs T/T_c for the Gorter-Casimir theory and for the present theory. Experimental values for tin are shown for comparison. *Note added in proof.*—The plotted theoretical curve is incorrect very near T_c ; the intercept at T_c should be 2.52.

or with (3.39),

$$\left. \frac{dH_c}{dT} \right|_{T_c} = -\frac{1.82H_0}{T_c}. \quad (3.53)$$

When $\beta\epsilon_0 \gg 1$, the specific heat can be expressed in the form

$$\frac{C_{es}}{\gamma T_c} = \frac{3}{2\pi^2} \left(\frac{\epsilon_0}{kT_c} \right)^3 \left(\frac{T_c}{T} \right)^2 [3K_1(\beta\epsilon_0) + K_3(\beta\epsilon_0)] \approx 8.5e^{-1.44T_c/T}, \quad (3.54)$$

where K_n is the modified Bessel function of the second kind.

The ratio $C_{es}/(\gamma T_c)$ is plotted in Fig. 3 from (3.46) and compared with the T^3 law and the experimental values for tin. The agreement is rather good except near T_c where our specific heat is somewhat too small. The logarithm of the same ratio is plotted in Fig. 4 to bring out the experimental deviation from the T^3 law. The recent work of Goodman *et al.*²⁰ shows that the data for tin and vanadium fit the law:

$$C_{es}/(\gamma T_c) = ae^{-bT_c/T}, \quad (3.55)$$

with high accuracy for $T_c/T > 1.4$, where $a=9.10$ and $b=1.50$. These values are in good agreement with our results in this region, (3.54).

Thus we see that our theory predicts the thermodynamic properties of a superconductor quite accurately and in particular gives an exponential specific heat for $T/T_c \ll 1$ and explicitly exhibits a second-order phase transition in the absence of a magnetic field.

and the jump in specific heat becomes

$$\left. \frac{C_{es} - \gamma T_c}{\gamma T_c} \right|_{T_c} = 1.52. \quad (3.50)$$

The Gorter-Casimir model gives 2.00 and the Koppe theory⁹ gives 1.71 for this ratio. The experimental data in general range between our value and 2.00.

The initial slope of the critical-field curve at the transition temperature is given by the thermodynamic relation

$$\left. \frac{T_c}{4\pi} \left(\frac{dH_c}{dT} \right)^2 \right|_{T_c} = (C_s - C_n) \Big|_{T_c}. \quad (3.51)$$

With use of (3.47) this becomes

$$\left. \frac{1}{\gamma} \left(\frac{dH_c}{dT} \right)^2 \right|_{T_c} = 19.4, \quad (3.52)$$

$^{\circ}\text{K}$ vs
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