Superconductivity of a Charged Ideal Bose Gas

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It is shown that an ideal gas of charged bosons exhibits the essential equilibrium features of a superconductor. The onset of Bose-Einstein condensation marks the transition temperature T_c. Below T_c a Meissner-Ochsenfeld effect is exhibited which is described in a very good approximation by London's equation.

The singular nature of the condensed ideal Bose gas exhibits itself in a space dependence of the London constant λ, determined by the boundary conditions on the wave function. It is shown that the electrostatic repulsion between the bosons compensates this effect and leads to a spatially constant λ, independently of the boundary conditions.

The critical field $H_c(T)$ is determined and found to be related to the penetration depth $d(T)$ by

$$H_c=\hbar c/2ed^2$$

(e being the boson charge).

The $B(H)$ law is different from the one usually assumed for actual superconductors. Corresponding changes occur in the thermodynamical relation.

A comparison with superconducting metals is made. The main conclusion is that if superconductivity in metals is due to the concurrence of bosons, then the number of these bosons must be strongly temperature-dependent below T_c.

1. INTRODUCTION

SO far, no molecular theory of superconductivity has been found. The most successful attempts in this direction have been made by Froehlich and Bardeen[1] on the assumption that the occurrence of this phenomenon is due to the interaction of the conduction electrons with lattice vibrations. This assumption led to reasonable estimates of the energy values involved and was thus able to explain the isotope effect.[2] However, it has so far not been possible to show that a strong enough lattice-electron interaction can account for the characteristic equilibrium phenomena of superconductivity, namely the phase transition and the Meissner-Ochsenfeld effect. In the weak-coupling approximation employed by Froehlich[1] these effects certainly do not occur.[3]

The effects of the lattice-electron interaction in any other than the weak-coupling approximation are very complex, and it is difficult to foresee which will be the characteristic feature responsible for a transition to the superconducting state. This holds especially because until recently no simple physical model was known which exhibits the equilibrium properties of a superconductor and which could serve as a lead in the search for the real phenomenon.

Such a model has recently been pointed out by the author[4]: it is the ideal gas of charged bosons. The purpose of this paper is to prove this assertion and to discuss the detailed properties of this model.

The fact that an ideal Bose gas exhibits a thermodynamic transition point of the second kind[5] is well known[6] and need not be dealt with here. The transition temperature T_c is given by

$$kT_c=4\pi\frac{\hbar^2}{2m}\left[\frac{n}{\zeta(\frac{3}{2})}\right]^{\frac{2}{3}}, \tag{1.1}$$

where m is the mass of the bosons, n their density, k the Boltzmann constant and

$$\zeta(s)=\sum_{n=1}^{\infty}n^{-s}\quad(s>1) \tag{1.2}$$

is the Riemann ζ function.

In contrast to real superconductors, the specific heat is continuous through the transition temperature, and only its derivative exhibits a jump. (Such a transition is often called "of the third kind.")

At temperature $T<T_c$ a finite fraction n_s of the total boson density n is condensed in the ground state, the remaining part $n_n=n-n_s$ forms a normal Bose gas with chemical potential $\mu=0$.[7] The densities in the two phases are given by

$$n_n=n(T/T_c)^{\frac{3}{2}}, \tag{1.3}$$

$$n_s=n[1-(T/T_c)^{\frac{3}{2}}]. \tag{1.4}$$

An indication that at the condensation point an ideal charged Bose gas becomes superconducting is found in computing its magnetic susceptibility. The magnetic

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[1] H. Froehlich, Phys. Rev. **79**, 845 (1950); J. Bardeen, Revs. Modern Phys. **23**, 261 (1951), and references given there.

[2] E. Maxwell, Phys. Rev. **78**, 477 (1950); **79**, 173 (1950); Reynolds, Serin, Wright, and Nesbitt, Phys. Rev. **78**, 487 (1950); Serin, Reynolds, and Nesbitt, Phys. Rev. **78**, 813 (1950).

[3] M. R. Schafroth, Helv. Phys. Acta **24**, 645 (1951).

[4] M. R. Schafroth, Phys. Rev. **96**, 1149 (1954).

[5] We call any transition without latent heat "of the second kind."

[6] A. Einstein, Ber. Berl. Akad. 261 (1924); 3 (1925); F. London, Phys. Rev. **54**, 947 (1938); B. Kahn and G. E. Uhlenbeck, Physica **5**, 399 (1938).

[7] These statements hold in the limit of infinitely large volume G, i.e., neglecting G^{-1} compared to n. For finite volumes, μ is of the order G^{-1}, depending on the shape of the volume, and there is no sharp transition.

susceptibility is defined by

$$M=\chi H,$$

where H is the applied field; what is actually computed, however, is a quantity χ' defined by

$$M=\chi' H',$$

where H' is the "acting" field. The relation between H and H' requires special attention; this point will be discussed in Sec. 5.

For an ideal charged Bose gas, χ' tends to $-\infty$ on approaching condensation. Quite generally, for an ideal gas, χ' is given by[8]

$$\chi'=-\tfrac{1}{6}\mu_0{}^2 n\langle E^{-1}\rangle_{\text{Av}}, \tag{1.5}$$

where $\mu_0=eh/2mc$ is Bohr's magneton $n=N/V$ the density of particles, and $\langle E^{-1}\rangle_{\text{Av}}$ is the average of the reciprocal kinetic energy of a particle over the distribution function. For a Bose gas this is

$$N\langle E^{-1}\rangle_{\text{Av}}=\frac{(2m)^{\frac{3}{2}}}{4\pi^2\hbar^3}\int_0^\infty d\epsilon\epsilon^{-\frac{1}{2}}\{\exp[\alpha(\epsilon-\mu)]-1\}^{-1} \tag{1.6}$$

[$\alpha=1/kT$; $\mu=$chemical potential ($\mu<0$)]. For small $|\mu|$ this is of the order $|\mu|^{-\frac{1}{2}}$; on approaching condensation, $\mu\rightarrow 0$ and therefore $\chi'\rightarrow\infty$. (For a finite volume, μ and χ' become volume- and shape-dependent, and (1.5) is no longer valid.)

To establish the Meissner-Ochsenfeld effect, however more is needed. The current density induced by an *inhomogeneous* magnetic field has to be studied. The ensuing relation between current and field together with Maxwell's equation

$$\text{curl}\mathbf{H}=(4\pi/c)\mathbf{i} \tag{1.7}$$

must then lead to an expulsion of the field from the system.

It is advantageous to expand the magnetic field in terms of a complete orthonormal set of functions appropriate to the shape of the volume under study. For a cubical box of volume G with periodical boundary conditions, which is the easiest volume to work with, these eigenfunctions are plane waves

$$\psi_{\mathbf{q}}(\mathbf{x})=G^{-\frac{1}{2}}\exp(i\mathbf{q}\cdot\mathbf{x}). \tag{1.8}$$

We restrict ourselves to weak fields, so that the relation between field and induced current can be taken as linear. In view of the translational symmetry of the particular volume chosen, this relation between current density $\mathbf{i}(\mathbf{x})$ and vector potential $\mathbf{A}(\mathbf{x})$ takes the simple general form

$$i_\mu(\mathbf{x})=\sum_{\nu=1}^{3}\int_G d^3\mathbf{x}' K_{\mu\nu}(\mathbf{x}-\mathbf{x}')A_\nu(\mathbf{x}'). \tag{1.9}$$

[8] See reference 3, appendix; see also Sec. 2 of the present paper.

In terms of the Fourier transforms [i.e., the coefficients in an expansion in terms of (1.8)], this becomes

$$i_\mu(\mathbf{q})=\sum_{\nu=1}^{3}K_{\mu\nu}(\mathbf{q})A_\nu(\mathbf{q}). \tag{1.10}$$

Gauge invariance requires[3]

$$K_{\mu\nu}(\mathbf{q})=(q_\mu q_\nu-\delta_{\mu\nu}q^2)K(q^2). \tag{1.11}$$

Normal diamagnetism corresponds to a $K(q^2)$ regular for small values of q:

$$K(q^2)=-c\chi'+O(q^2) \tag{1.12}$$

(c is the velocity of light). A pole at $q=0$ gives a Meissner-Ochsenfeld effect; in particular, the form

$$K(q^2)=1/\lambda cq^2 \tag{1.13}$$

is equivalent to the London[9] equation

$$-\lambda c\,\text{curl}\mathbf{i}=\mathbf{H}. \tag{1.14}$$

The main result of this paper is that the ideal Bose gas below its condensation point obeys London's equation (1.14) with

$$\lambda^{-1}=(e^2/m)n_s, \tag{1.15}$$

where n_s is the density of condensed particles (1.4). This holds except for additional terms in $K(q^2)$ proportional to $|\mathbf{q}|^{-1}$ which are, however, practically negligible in all cases.

Special attention has to be devoted to the influence of the boundary condition on the boson wave functions. The calculations in Secs. 2 and 3 are devoted to the simplest case of a cube with periodical boundary condition. As, however, the occurrence of the Meissner-Ochsenfeld effect is due to the condensed bosons, i.e., to a finite fraction of the total particle density occupying a state which extends over the whole volume, there is no reason to assume that the relation between current density and field is independent of the boundary condition. A simplified calculation is carried through in Sec. 4; it takes into account only the contribution of the condensed bosons, relying on the discussion in Sec. 3 that the noncondensed particles do not contribute significantly. The result is that indeed the London equation (1.14) has to be replaced in general by

$$-c\,\text{curl}(\lambda\mathbf{i})=\mathbf{H}, \tag{1.14'}$$

with

$$\lambda^{-1}=(e^2/m)n_s(\mathbf{x}), \tag{1.15'}$$

where now $n_s(\mathbf{x})$, the local density of bosons, is in general a function of position, depending upon the boundary condition. For a cube of volume $G=L^3$ with perfectly reflecting walls,

$$n_s(x)=n_s{}^0\cdot\frac{8}{G}\sin^2\frac{\pi x}{L}\sin^2\frac{\pi y}{L}\sin^2\frac{\pi z}{L}, \tag{1.16}$$

[9] F. London, *Superfluids I* (John Wiley and Sons, Inc., New York, 1950).

where n_s^0 is the average density of condensed bosons. This marked dependence of the Meissner-Ochsenfeld effect on the boundary conditions reflects the fact that the ideal Bose gas without any interactions whatsoever is a highly idealized system. However, it will be shown in Sec. 4 that this arbitrariness can be removed by including, in a self-consistent way, the Coulomb interaction between the bosons. In this case, the London equation (1.14) is restored.

What the relation of the present model to the future theory of superconductivity will be, is hard to foresee. It seems, however, unlikely that there should be no close relation between the two, especially in view of the fact that the Bose-Einstein condensation of a boson gas—which gives the transition to the superconducting state of the model—is a very singular and unique phenomenon which is responsible also for the other spectacular low-temperature phenomenon: superfluidity.[10] It seems therefore reasonable to expect superconductivity in metals to be due to the occurrence of charge-carrying bosons in the metal. The author has recently suggested[11] that these "bosons" might be resonant two-electron states. A crude theory of chemical equilibrium between these "bosons" and free electrons then gives results which agree qualitatively (although not quantitatively) with the observed behavior. No detailed discussion of this suggestion, however, will be given in this paper.

2. INDUCED CURRENT DENSITY

In order to calculate the current density induced by a weak inhomogeneous magnetic field in a charged ideal gas, we use perturbation theory on the distribution function as developed earlier.[3,12] As we are considering inhomogeneous fields, perturbation theory on the magnetic field is here permitted, in contrast to the case of homogeneous fields, where arbitrarily small fields produce qualitative changes in the wave functions of the electrons, as soon as the volume is big enough. Also, perturbation theory on the distribution function does not suffer from the limitations of perturbation theory on the energy levels in the case of complete or near degeneracies.[12,13]

A function $F_0(\Lambda_0+\epsilon\Lambda_1)$ of an operator $\Lambda\equiv\Lambda_0+\epsilon\Lambda_1$ is expanded in powers of ϵ in the representation in which Λ_0 is diagonal

$$\Lambda_0|n\rangle=\lambda_n|n\rangle, \tag{2.1}$$

by

$$\langle n|F_0(\Lambda_0+\epsilon\Lambda_1)|m\rangle=\delta_{nm}F_0(\lambda_n)+\epsilon\langle n|\Lambda_1|m\rangle F_1(\lambda_n,\lambda_m)+O(\epsilon^2), \tag{2.2}$$

where

$$F_1(\lambda_n,\lambda_m)=\frac{F_0(\lambda_n)-F_0(\lambda_m)}{\lambda_n-\lambda_m}. \tag{2.3}$$

We take Λ_0 to be the Hamiltonian of a free particle

$$\Lambda_0\equiv H_0=(1/2m)\mathbf{p}^2, \tag{2.4}$$

and $\epsilon\Lambda_1$ to be the perturbation due to a magnetic field

$$\epsilon\Lambda_1\equiv H'=-\frac{e}{2mc}\{\mathbf{p}\cdot\mathbf{A}(\mathbf{x})+\mathbf{A}(\mathbf{x})\cdot\mathbf{p}\}+O(\mathbf{A}^2), \tag{2.5}$$

where $\mathbf{A}(\mathbf{x})$ is the vector potential of the magnetic field in an arbitrary gauge. $F_0(H)(H=H_0+H')$ is the distribution function, i.e., for a Bose gas

$$F_0(H)=[e^{\alpha(H-\mu)}-1]^{-1} \tag{2.6}$$

($\alpha=1/kT$, $\mu<0$ chemical potential).

The average current density in thermal equilibrium is then, up to terms linear in the magnetic field[14]

$$\mathbf{i}(\mathbf{x})=-\frac{e^2}{m^2c}\frac{1}{G}\sum_{\mathbf{p},\mathbf{q}}(\mathbf{p}\cdot\mathbf{A}(\mathbf{q}))\mathbf{p}\times\exp(-i\mathbf{q}\cdot\mathbf{x})\cdot F_1\left[\frac{(\mathbf{p}+\mathbf{q}/2)^2}{2m},\frac{(\mathbf{p}-\mathbf{q}/2)^2}{2m}\right]-\frac{e^2}{mc}\frac{1}{G}\mathbf{A}(\mathbf{x})\sum_{\mathbf{p}}F_0\left(\frac{\mathbf{p}^2}{2m}\right). \tag{2.7}$$

Here $\mathbf{A}(\mathbf{q})$ is the Fourier transform of $\mathbf{A}(\mathbf{x})$:

$$\mathbf{A}(\mathbf{x})=\sum_{\mathbf{p}}\mathbf{A}(\mathbf{q})\exp(-i\mathbf{q}\cdot\mathbf{x}). \tag{2.8}$$

Simplifying (2.7) using

$$\sum_{\mathbf{p}}F_0\left(\frac{\mathbf{p}^2}{2m}\right)=N, \tag{2.9}$$

we get

$$i_\mu(\mathbf{x})=-\frac{e^2}{mc}\frac{N}{G}A_\mu(\mathbf{x})-\frac{e^2}{mc}\frac{1}{G}\sum_{\nu=1}^{3}\sum_{\mathbf{q}}I_{\mu\nu}(\mathbf{q})A_\nu(\mathbf{q})\exp(-i\mathbf{q}\cdot\mathbf{x}), \tag{2.10}$$

where

$$I_{\mu\nu}(\mathbf{q})=\sum_{\mathbf{p}}\frac{p_\mu p_\nu}{(\mathbf{p}\cdot\mathbf{q})}\left[F_0\left(\frac{(\mathbf{p}+\mathbf{q}/2)^2}{2m}\right)-F_0\left(\frac{(\mathbf{p}-\mathbf{q}/2)^2}{2m}\right)\right], \tag{2.11}$$

and where use has been made of (2.3).

In order to evaluate $I_{\mu\nu}(\mathbf{q})$ we exploit the fact that it depends only on the vector $\mathbf{q}$, so that it must have the

[10] F. London, Phys. Rev. **54**, 947 (1938); S. T. Butler and M. H. Friedman, Phys. Rev. **98**, 287 (1955); J. M. Blatt and S. T. Butler, Phys. Rev. **96**, 1149 (1954).

[11] M. R. Schafroth, Phys. Rev. **96**, 1442 (1954); see also C. J. Gorter, *Progress in Low Temperature Physics* (Interscience Publishers, Inc., New York, 1955), Vol. I.

[12] M. J. Buckingham and M. R. Schafroth, Proc. Phys. Soc. (London) **A67**, 828 (1954).

[13] R. Peierls, Z. Physik **80**, 763 (1933).

[14] We put $\hbar=1$ throughout this section for convenience of notation.

form

$$I_{\mu\nu}(\mathbf{q})=a(q^2)q_\mu q_\nu+b(q^2)q^2\delta_{\mu\nu}. \quad (2.12)$$

Then:

$$\sum_\mu I_{\mu\mu}=(a+3b)q^2\equiv I_0,$$
$$\sum_{\mu\nu} I_{\mu\nu}q_\mu q_\nu=(a+b)q^4\equiv I_1, \quad (2.13)$$

where now

$$I_0=\sum_\mathbf{p}\frac{\mathbf{p}^2}{(\mathbf{p}\cdot\mathbf{q})}\left\{F_0\left[\frac{(\mathbf{p}+\mathbf{q}/2)^2}{2m}\right]-F_0\left[\frac{(\mathbf{p}-\mathbf{q}/2)^2}{2m}\right]\right\},$$
$$I_1=\sum_\mathbf{p}(\mathbf{p}\cdot\mathbf{q})\left\{F_0\left[\frac{(\mathbf{p}+\mathbf{q}/2)^2}{2m}\right]-F_0\left[\frac{(\mathbf{p}-\mathbf{q}/2)^2}{2m}\right]\right\}. \quad (2.14)$$

I_1 gives by straightforward evaluation

$$I_1=\sum_\mathbf{p}\left[\left(\mathbf{p}-\frac{\mathbf{q}}{2}\right)\mathbf{q}-\left(\mathbf{p}+\frac{\mathbf{q}}{2}\right)\mathbf{q}\right]F_0\left(\frac{\mathbf{p}^2}{2m}\right)=-q^2\sum_p F_0\left(\frac{\mathbf{p}^2}{2m}\right)$$

or

$$I_1=-q^2N. \quad (2.15)$$

Using this, one finds from (2.12) and (2.13)

$$I_{\mu\nu}(\mathbf{q})=\tfrac{1}{2}(I_0+N)\left(\delta_{\mu\nu}-\frac{q_\mu q_\nu}{q^2}\right)-\frac{N}{q^2}q_\mu q_\nu,$$

and upon inserting into (2.10)

$$i_\mu(\mathbf{x})=-\frac{e^2}{mc}\frac{1}{G}\sum_{\nu=1}^{3}\sum_\mathbf{q}A_\nu(\mathbf{q})\exp(-i\mathbf{q}\cdot\mathbf{x})\times\tfrac{1}{2}(I_0+3N)\left(\delta_{\mu\nu}-\frac{q_\mu q_\nu}{q^2}\right), \quad (2.16)$$

which exhibits gauge invariance explicitly. Comparison with (1.10) and (1.11) shows

$$K(q^2)=\frac{e^2}{2mc}\frac{1}{G}\frac{I_0+3N}{q^2}. \quad (2.17)$$

We now proceed to evaluate I_0:

(1) For a noncondensed Bose gas (as well as for a Fermi gas) the distribution function is regular at $\mathbf{p}^2=0$ so that for small $|\mathbf{q}|$ we may expand the summand in (2.14) in powers of $\mathbf{q}$. We thus write

$$F_0\left(\frac{(\mathbf{p}+\mathbf{q}/2)^2}{2m}\right)-F_0\left(\frac{(\mathbf{p}-\mathbf{q}/2)^2}{2m}\right)=\frac{\mathbf{p}\cdot\mathbf{q}}{m}F_0'\left(\frac{\mathbf{p}^2}{2m}\right)+\frac{\mathbf{p}\cdot\mathbf{q}}{m}\frac{\mathbf{q}^2}{8m}F_0''\left(\frac{\mathbf{p}^2}{2m}\right)+\tfrac{1}{3}\left(\frac{\mathbf{p}\cdot\mathbf{q}}{2m}\right)^3F_0'''\left(\frac{\mathbf{p}^2}{2m}\right)+O(\mathbf{q}^4), \quad (2.18)$$

where the dash indicates differentiation with respect to the energy $E=\mathbf{p}^2/2m$. The first term gives

$$I_{00}=2\sum_\mathbf{p}\frac{\mathbf{p}^2}{2m}F_0'\left(\frac{\mathbf{p}^2}{2m}\right),$$

which in turn, replacing sums by integrals, yields

$$I_{00}=\frac{G}{(2\pi)^3}2\int d^3\mathbf{p}\frac{\mathbf{p}^2}{2m}F_0'\left(\frac{\mathbf{p}^2}{2m}\right)=\frac{G}{4\pi^2}2(2m)^{\frac{3}{2}}\int_0^\infty dEE^{\frac{3}{2}}F_0'(E)$$

and by integration by parts

$$I_{00}=-\frac{G}{4\pi^2}3(2m)^{\frac{3}{2}}\int_0^\infty dEE^{\frac{1}{2}}F_0(E)=-3\sum_\mathbf{p}F_0\left(\frac{\mathbf{p}^2}{2m}\right),$$

or

$$I_{00}=-3N. \quad (2.19)$$

The remaining terms in (2.18) give similarly

$$I_{02}=\frac{\mathbf{q}^2}{12m}\sum_p\left(\frac{\mathbf{p}^2}{2m}\right)^{-1}F_0\left(\frac{\mathbf{p}^2}{2m}\right)=\frac{q^2}{12m}N\langle E^{-1}\rangle_{\text{Av}}, \quad (2.20)$$

so that

$$K(q^2)=\frac{e^2}{24m^2c}\frac{N\langle E^{-1}\rangle_{\text{Av}}}{G}+O(q^2), \quad (2.21)$$

i.e., we get the usual diamagnetism (1.5) of a gas of charged particles, but no Meissner effect.

(2) For a condensed Bose-gas, however, the distribution function is no longer regular at $\mathbf{p}^2=0$ and, therefore, the above procedure does not apply. The ground state is highly occupied (by N_s particles) and has to be treated separately[6]; for the other states one can use the usual Bose distribution with $\mu=0$; replacement of sums by integrals is justified.

We write

$$I_0=\sum_\mathbf{p}\left[\frac{(\mathbf{p}-\mathbf{q}/2)^2}{(\mathbf{p}-\mathbf{q}/2)\cdot\mathbf{q}}-\frac{(\mathbf{p}+\mathbf{q}/2)^2}{(\mathbf{p}+\mathbf{q}/2)\cdot\mathbf{q}}\right]F_0\left(\frac{\mathbf{p}^2}{2m}\right). \quad (2.22)$$

The noncondensed particles contribute

$$I_{0n}=\frac{G}{(2\pi)^3}\int d^3\mathbf{p}\left[\frac{(\mathbf{p}-\mathbf{q}/2)^2}{(\mathbf{p}-\mathbf{q}/2)\cdot\mathbf{q}}-\frac{(\mathbf{p}+\mathbf{q}/2)^2}{(\mathbf{p}+\mathbf{q}/2)\mathbf{q}}\right]\times\left[\exp\left(\alpha\frac{\mathbf{p}^2}{2m}\right)-1\right]^{-1}. \quad (2.23)$$

Care has to be taken here because, in transforming I_0 from the original form (2.14) to (2.22), singularities in the two terms under the sum which compensated in (2.14) have been separated, so that (2.23) contains singularities. A prescription for integrating over these singularities must therefore be given which ensures the equivalence of (2.14) and (2.23). It can be seen that it is a correct prescription in this sense to take the principal value in the integration over the angles in (2.23).

Performing the integration over the angles in (2.23) then yields

$$I_{0n}=4\pi\frac{G}{(2\pi)^3}\int_0^\infty dp\left[\frac{p}{q}\left(p^2-\frac{q^2}{4}\right)\times\log\left|\frac{p-q/2}{p+q/2}\right|-2p^2\right]\left[\exp\left(\alpha\frac{p^2}{2m}\right)-1\right]^{-1}$$

with $q=|\mathbf{q}|$.

The number of noncondensed bosons is

$$N_n\equiv N-N_s=\sum_{\mathbf{p}\neq 0}\left[\exp\left(\alpha\frac{\mathbf{p}^2}{2m}\right)-1\right]^{-1}=4\pi\frac{G}{(2\pi)^3}\int_0^\infty dp p^2\left[\exp\left(\alpha\frac{p^2}{2m}\right)-1\right]^{-1}$$

so that

$$I_{0n}+3N_n=4\pi\frac{G}{(2\pi)^3}\int_0^\infty dp\left[\frac{p}{q}\left(p^2-\frac{q^2}{4}\right)\times\log\left|\frac{p-q/2}{p+q/2}\right|+p^2\right]\times\left[\exp\left(\alpha\frac{p^2}{2m}\right)-1\right]^{-1}. \quad (2.24)$$

The contribution from the condensed particles is, from (2.22), for $p=0$:

$$I_{0s}=-N_s,$$

and

$$I_{0s}+3N_s=2N_s. \quad (2.25)$$

Thus finally, inserting (2.24) and (2.25) into (2.17) we get

$$K(q^2)=K_s(q^2)+K_n(q^2),$$

$$K_s(q^2)=\frac{e^2}{mc}\frac{N_s}{G}\frac{1}{q^2},$$

$$K_n(q^2)=\frac{e^2}{mc}\frac{1}{4\pi^2}\frac{1}{q^2}\int_0^\infty dp\left[\frac{p}{q}\left(p^2-\frac{q^2}{4}\right)\times\log\left|\frac{p-q/2}{p+q/2}\right|+p^2\right]\left[\exp\left(\alpha\frac{p^2}{2m}\right)-1\right]^{-1}. \quad (2.26)$$

It is seen that the integral in the second term vanishes for $q\rightarrow 0$, so that $K_s(q^2)$ cannot be compensated by $K_n(q^2)$. $K_s(q^2)$, the contribution from the condensed bosons, has exactly the form (1.13) of London's equation. $K_n(q^2)$ stems from the uncondensed particles and vanishes at absolute zero so that for $T=0$ London's equation holds exactly. At finite temperatures, $K_n(q^2)$ can be written[15]

$$K_n(q^2)=\frac{e^2}{2mc}\frac{1}{4\pi^2}\frac{(2mkT)^{\frac{3}{2}}}{\hbar^3q^2}k\left(\frac{\hbar q}{2(2mkT)^{\frac{1}{2}}}\right), \quad (2.27)$$

where

$$k(z)\equiv\int_0^\infty dx\left[\frac{x}{2z}(x^2-z^2)\log\left|\frac{x-z}{x+z}\right|+x^2\right]\frac{1}{e^{x^2}-1}. \quad (2.28)$$

It is shown in Appendix I that the expansion of $k(z)$ for small $|z|$ is

$$k(z)=\frac{\pi^2}{4}z+\frac{\sqrt{\pi}}{3}\zeta(\tfrac{1}{2})z^2+O(z^4). \quad (2.29)$$

The second and higher terms in this expansion give simply a normal diamagnetism (1.12), whereas the first term still yields a pole of $K_n(q^2)$ at $q=0$:

$$K_n(q^2)=\frac{1}{32}\frac{e^2}{mc}\frac{2mkT}{\hbar^2q}+O(1). \quad (2.30)$$

Thus finally, from (2.26) and (2.30):

$$K(q^2)=\frac{e^2}{mc}\left[\frac{N_s}{G}\frac{1}{q^2}+\frac{1}{32}\frac{2mkT}{\hbar^2q}+O(1)\right]. \quad (2.31)$$

3. DISCUSSION OF THE KERNEL $K(q^2)$

As pointed out earlier, the form (2.31) of $K(q^2)$ shows that the relation between field and induced current does not take the simple London form (1.13), but it is rather an integral relationship. It will be shown, however, that $K_n(q^2)$ is in general negligible as compared to $K_s(q^2)$, i.e., that London's equation holds with a very good accuracy for the condensed Bose gas.

One has to judge the relative importance of the two terms in (2.31) for values of $q\sim d^{-1}$, where d is the penetration depth. We take for d the value given by the London term $K_s(q^2)$ alone, which is correct as long as $K_n(q^2)$ is indeed negligible, i.e., we write[9]

$$d=(mc^2/4\pi n_se^2)^{\frac{1}{2}}. \quad (3.1)$$

$K_n(q^2)$ is then negligible compared to $K_s(q^2)$ as long as

$$n_s\gg\frac{\pi}{256}\frac{e^2}{mc^2}\left(\frac{2mkT}{\hbar^2}\right)^2. \quad (3.2)$$

Using (1.4) this yields:

$$1-(T/T_c)^{\frac{3}{2}}\gg\frac{\pi^3}{16[\zeta(\frac{3}{2})]^{4/3}}\frac{e^2}{mc^2}n^{\frac{1}{3}}. \quad (3.3)$$

This shows that the deviation of the magnetic behavior of a Bose gas from the pure London equation is negligible as long as the mean distance between bosons

[15] We reinsert here for convenience the constant $\hbar$ which was put $=1$ before.

($n^{-\frac{1}{3}}$) is large compared to the "classical boson radius" e^2/mc^2. Fitting, e.g., n through (1.1) to a transition temperature of a few degrees Kelvin and taking the mass and charge of the bosons to be of the order of the mass and charge of electrons, the right-hand side of (3.3) is of the order 10^{-8}.

We therefore conclude that for all practical purposes the condensed Bose gas obeys London's equation

$$-\lambda c\, \mathrm{curl}\,\mathbf{i}=\mathbf{H}, \tag{3.4}$$

with

$$\lambda^{-1}=(e^2/m)n_s, \tag{3.5}$$

n_s being the number of condensed bosons per unit volume.

The penetration depth d is given by (3.1), and its temperature dependence is

$$d=d_0[1-(T/T_c)^{\frac{3}{2}}]^{-\frac{1}{2}}, \tag{3.6}$$

with

$$d_0=(mc^2/4\pi e^2 n)^{\frac{1}{2}} \tag{3.7}$$

n being the total boson density.

In the temperature region in which (3.3) is violated the penetration depth becomes larger than the value (3.6). It can be shown that the definition of the penetration depth given, e.g., by Pippard[16] is equivalent to the following definition in terms of $f(q)=q^2K(q^2)$:

$$d^{-1}=\frac{2}{\pi}\int_0^\infty dq\frac{(4\pi/c)f(0)}{q^2+(4\pi/c)f(q)}. \tag{3.8}$$

This shows that the $1/q$-term as well as a normal diamagnetism [(1.12) with $\chi'<0$] tend to increase the penetration depth. One finds from (3.8) that, as $T\rightarrow T_c$, d actually becomes infinite like

$$\{(1-T/T_c)\log(1-T/T_c)\}^{-1},$$

instead of the behavior $(1-T/T_c)^{-\frac{1}{2}}$ which arises out of (3.6).

4. INFLUENCE OF THE BOUNDARY CONDITION

The complete analysis carried out in Sec. 2 for the cubical volume with periodical boundary conditions becomes very cumbersome if applied to other volumes. We are therefore going to use a simplified approach to study the dependence on the boundary conditions. A convenient volume to use is a cube of volume L^3 with walls at $x=0$ and $x=L$; in the y- and z-directions we shall apply periodical boundary conditions. This volume, though still artificial, allows a study of the effect of walls in a simple way without introducing spurious complications due to corners, etc. In addition, we restrict ourselves to an inhomogeneous magnetic field depending on x alone; from $\mathrm{div}B=0$ it follows that, if we exclude a homogeneous component parallel to x, $\mathbf{B}$ must be parallel to the wall; we take $\mathbf{B}$ to lie in the y-direction. $\mathbf{B}$ can then be described by a vector potential $\mathbf{A}$ in a gauge where

$$\mathrm{div}\mathbf{A}=0, \tag{4.1}$$

and on the surface

$$A_{\mathrm{normal}}=0. \tag{4.2}$$

This entails

$$A_x=A_y=0;\quad A_z=A(x). \tag{4.3}$$

If we now neglect the contributions of the noncondensed bosons, our problem reduces to calculating the first-order perturbation induced by a vector potential (4.3) in the current density carried by the ground state.

The states of the system are given by

$$\psi_{k_1k_2n}(\mathbf{x})=(1/L)e^{i(k_1y+k_2z)}\varphi_n(x), \tag{4.4}$$

where $k_i=(2\pi/L)s_i$, s_i being integers, and $\varphi_n(x)$ are normalized one-dimensional free-particle wave functions in the interval $0\leq x\leq L$. They are determined by boundary conditions at $x=0$ and $x=L$. As it is just the effect of these boundary conditions that we are interested in, we are going to leave them open for the time being.

The ground-state wave function is

$$\psi_{000}(\mathbf{x})=(1/L)\varphi_0(x), \tag{4.5}$$

and the local density of condensed bosons is

$$n_s(\mathbf{x})=Ln_s^0|\varphi_0(x)|^2,\qquad n_s^0=L^{-3}\int d^3\mathbf{x}\,n_s(\mathbf{x}). \tag{4.6}$$

The perturbation operation in the Hamiltonian due to the field (4.3) is

$$H^1=-\frac{e\hbar}{mc}(1/i)A(x)\frac{\partial}{\partial z}. \tag{4.7}$$

The matrix element which determines the perturbation of the ground-state wave function is

$$(k_1k_2n|H^1|000), \tag{4.8}$$

and this is *identically zero*, irrespective of the form of $\varphi_0(x)$, i.e., for all kinds of boundary conditions at the walls.

The current density

$$\mathbf{i}(\mathbf{x})=n_s^0\left\{\frac{e\hbar}{2mi}\left(\frac{\partial\psi^*}{\partial\mathbf{x}}\psi-\psi^*\frac{\partial\psi}{\partial\mathbf{x}}\right)-\frac{e^2}{mc}\mathbf{A}(\mathbf{x})|\psi(\mathbf{x})|^2\right\}, \tag{4.9}$$

therefore becomes, using (4.6)

$$\mathbf{i}(\mathbf{x})=-(e^2/mc)\mathbf{A}(\mathbf{x})n_s(\mathbf{x}), \tag{4.10}$$

which obeys (1.14′) and (1.15′).

This is exactly the way in which London[9] predicted superconductivity to arise: A long-range order (due here to the nature of the condensed state) prevents the wave function of the superconducting particles from adapting itself to the magnetic field. It must, however, be noted

[16] A. B. Pippard, Proc. Roy. Soc. (London) **A216**, 547 (1953).

that such an argument is valid only if the expression (4.9) for the current density holds, which will in general not be true if the long-range order is due to some interactions. It has, for example, been shown very generally for weak-coupling interactions that any such tendency of the wave function to "stiffen" in that way will be countered by extra terms in the current density which nullify the effect.[3,17] In the Bose gas, however, the long-range order is a purely statistical effect, so that (4.9) holds; and therefore London's argument goes through.

We now specify boundary conditions:

(a) For perfectly reflecting walls,

$$\psi(0)=\psi(L)=0, \tag{4.11}$$

we have

$$\varphi_0(x)=(2/L)^{\frac{1}{2}}\sin(\pi x/L), \tag{4.12}$$

and

$$n_s(x)=n_0{}^s(2/L)\sin^2(\pi x/L). \tag{4.13}$$

Inserted into (4.10), this gives a law of penetration which depends on the size of the container, in disagreement with experimental facts.

(b) The boundary condition

$$\left(\frac{\partial\psi}{\partial x}\right)_{x=0}=\left(\frac{\partial\psi}{\partial x}\right)_{x=L}=0, \tag{4.14}$$

or the periodicity condition

$$\psi(0)=\psi(L),\qquad \left(\frac{\partial\psi}{\partial x}\right)_{x=0}=\left(\frac{\partial\psi}{\partial x}\right)_{x=L}, \tag{4.15}$$

on the other hand yield

$$\varphi_0(x)=L^{-\frac{1}{2}}, \tag{4.16}$$

$$n_s(x)=n_s{}^0, \tag{4.17}$$

i.e., the London equation (1.14) holds.

As mentioned in the introduction, this strong dependence of the results on the boundary conditions is due to the fact that the ideal Bose gas with no interaction whatsoever between particles is physically quite unrealistic. It will, however, still provide a useful model of a superconductor if one chooses artificially the boundary condition (4.14) which yields a uniform local density $n_s(\mathbf{x})$ of condensed particles for any shape of the volume.

By a qualitative argument we shall now show that this is, indeed, the proper procedure if one takes into account the Coulomb repulsion between particles.

In order to include the Coulomb interaction between bosons in a self-consistent way, we shall treat the particles as moving in a potential $V(x)$. $V(x)$ is related by Poisson's equation to the local charge density of the bosons; a uniform background charge has to be subtracted to make the whole system electrically neutral. The self-consistent equations for the wave function φ of the condensed state and the potential $V(x)$ are

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi}{dx^2}+[V(x)-E]\varphi(x)=0, \tag{4.18}$$

$$\frac{d^2V}{dx^2}+4\pi e^2 n_s{}^0(L|\varphi(x)|^2-1)=0. \tag{4.19}$$

In (4.19), $\rho_s=e^2n_s{}^0L|\varphi|^2$ is the charge density of the condensed bosons, whereas $\rho_n=-e^2n_s$ is the charge density of the uniform background and of the noncondensed particles.[18] E is the energy shift of the state $\varphi(x)$ due to the Coulomb interaction; it is linked with the normalization condition

$$\int_0^L dx|\varphi(x)|^2=1, \tag{4.20}$$

since the system (4.18), (4.19) is nonlinear.

The system (4.18), (4.19) has to be solved subject to the boundary conditions

$$\varphi(0)=\varphi(L)=0,\qquad V(0)=V(L)=0, \tag{4.21}$$

and the normalization condition (4.20). We are only interested in the ground-state solution, i.e., the one for which $\varphi(x)$ has no nodes. This excludes an oscillatory behavior of $\varphi(x)$ and therefore, through (4.19), of $V(x)$. Furthermore, $\varphi(x)$ cannot be appreciably different from its average value $L^{-\frac{1}{2}}$ over large regions (i.e., regions comparable to L), since this would lead to a building-up of $V(x)$ through (4.19), which in turn contradicts (4.18). We therefore expect $\varphi(x)$ to be practically equal to $L^{-\frac{1}{2}}$ throughout most of the range $0<x<L$, with a small region near the boundaries where it drops to its boundary value zero. We are now going to estimate this region near the boundary and show that the picture of the solution we thus get is indeed consistent.

We therefore put

$$\varphi(x)=L^{-\frac{1}{2}},\quad \lambda<x<L-\lambda,\qquad V(x)=V_0. \tag{4.22}$$

(4.22) is consistent with (4.18), (4.19) if we put $E=V_0$; V_0 is, therefore, just the energy shift of the ground-state due to the Coulomb repulsion.

The normalization condition (4.21) now requires that the average value of $|\varphi(x)|^2$ in the boundary regions $0<x<\lambda$ and $L-\lambda<x<L$ be equal to L:

$$\int_0^\lambda dx|\varphi(x)|^2=\lambda/L. \tag{4.23}$$

[17] M. R. Schafroth, Nuovo cimento 9, 291 (1952).

[18] Strictly, the charge density of the noncondensed bosons is not uniform if $V(x)$ is not constant. However, ρ_n is much less sensitive to $V(x)$ than the density ρ_s of condensed bosons, and since, as we shall show, the resulting $V(x)$ tends to be smoothed out, the approximation $\rho_n=$ constant is sufficient for our purpose.

This means that $\varphi(x)$ must rise from its value $\varphi(0)=0$ to a peak and then drop to the value $\varphi(\lambda)=L^{-\frac{1}{2}}$, and by symmetry, similarly near $x=L$. (4.19) then shows that $V(x)$ rises from $V(0)=0$ to a value

$$V_0 \equiv V(\lambda) \approx n_s^0 \cdot e^2 \cdot \lambda^2. \tag{4.24}$$

(4.18) now requires that

$$\hbar^2/2m\lambda^2 \approx E - V(0) = V(\lambda) - V(0) \approx n_s^0 e^2 \lambda^2. \tag{4.25}$$

Consistency is thus achieved for a λ of the order of magnitude

$$\lambda^4 \approx \hbar^2/me^2 n_s^0. \tag{4.26}$$

Using (3.1) to relate n_s^0 to the penetration depth d we find

$$\lambda/d \approx \left(\frac{\hbar/mc}{d}\right)^{\frac{1}{2}}. \tag{4.27}$$

For bosons of a mass comparable to or larger than the electron mass the right-hand side is always very small, so that the layer λ can always be neglected for calculations about superconducting phenomena. For our purposes, therefore, the Bose gas including Coulomb interaction behaves like an ideal Bose gas with the artificial boundary condition

$$(\partial\psi/\partial n)_{\text{wall}} = 0. \tag{4.28}$$

(4.28) gives the correct ground state $\psi(x)=G^{-\frac{1}{2}}$ for all volumes; the contributions due to the higher states, i.e., the contributions of the noncondensed bosons, are not affected by the choice of the boundary condition anyway, apart from pure surface effects.

The strong flattening of the ground-state wave function due to the Coulomb repulsion between particles may be surprising at first sight. It should be noted that this is again due to the high occupation of the ground state by the condensed particles: All of them contribute simultaneously to the potential $V(x)$ acting on any single one, and this cumulative effect is responsible for the high sensitivity of $V(x)$ to $\varphi(x)$ [through the factor $n_s^0 L$ in front of $|\varphi(x)|^2$ in (4.19)].

5. THE CRITICAL FIELD

Let us now consider a Bose gas in a cylindrical container in an "acting" homogeneous magnetic field H' parallel to the axis of the container. The grand canonical partition function $e^{-\alpha\Omega}$ can be worked out in a standard way[19] to give

$$\Omega = kT \frac{eH'}{2\hbar c} \frac{G}{2\pi^2} \int_{-\infty}^{+\infty} d\kappa \sum_{\nu=0}^{\infty} \times \log\left\{1 - \exp\left[-\alpha\left(\mu_0 H'(2\nu+1) + \frac{\hbar^2\kappa^2}{2m} - \mu\right)\right]\right\}, \tag{5.1}$$

where G is the volume of the container, $\mu_0 = eh/2mc$ Bohr's magneton, $\mu =$ the chemical potential, $\alpha = 1/kT$.

The number of particles is given by

$$N = -\frac{\partial\Omega}{\partial\mu} = \frac{eH'}{2\hbar c} \frac{G}{2\pi^2} \int_{-\infty}^{+\infty} d\kappa \sum_{\nu=0}^{\infty} \left\{\exp\left[\alpha\left(\mu_0 H'(2\nu+1) + \frac{\hbar^2\kappa^2}{2m} - \mu\right)\right] - 1\right\}^{-1}. \tag{5.2}$$

The free energy is

$$F = \Omega + \mu N. \tag{5.3}$$

The chemical potential μ is here no longer restricted to negative values as in the absence of a magnetic field, but can take values up to

$$\mu_{\max} = +\mu_0 H'. \tag{5.4}$$

(5.1) and (5.2) can be brought into a more tractable form by expanding the integrands in powers of $\exp\{-\alpha[\mu_0 H'(2\nu+1) + (\hbar^2\kappa^2/2m) - \mu]\}$ and interchanging summation and integration; this yields

$$\omega \equiv \frac{\Omega}{G} = -kTn_0 \frac{1}{\zeta(\frac{3}{2})} \sum_{\nu=1}^{\infty} \frac{e^{\alpha\mu\nu}}{\nu^{5/2}} \frac{\alpha\mu_0 H'\nu}{\sinh(\alpha\mu_0 H'\nu)}, \tag{5.5}$$

$$n \equiv \frac{N}{G} = n_0 \frac{1}{\zeta(\frac{3}{2})} \sum_{\nu=1}^{\infty} \frac{e^{\alpha\mu\nu}}{\nu^{\frac{3}{2}}} \frac{\alpha\mu_0 H'\nu}{\sinh(\alpha\mu_0 H'\nu)}. \tag{5.6}$$

Here,

$$n_0 = \zeta(\tfrac{3}{2}) \left(\frac{2mkT}{4\pi\hbar^2}\right)^{\frac{3}{2}} \tag{5.7}$$

is the maximum density of particles that can be accommodated outside the ground state in the Bose gas at temperature T without magnetic field.

On putting $H'=0$, (5.5) and (5.6) reduce to well-known expressions for the free Bose gas.

However, even arbitrarily small values of the magnetic field H' introduce qualitative changes. However small H', the sum in (5.6) can take arbitrarily large values, so that any density of bosons can be accommodated outside the ground state at all finite temperatures: *The Bose gas does not condense at any finite temperature if it is in a fixed homogeneous magnetic field.*[20]

An important question at this point is the precise nature of the "acting" field H'. The Lorentz relation

$$H' = H + (4\pi/3)M, \tag{5.8}$$

[19] W. Pauli, Solvay-Report 1930 (Gauthier-Villars, Paris, 1932), pp. 183–190 and H. A. Bethe and A. Sommerfeld, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), Vol. 24, Part 2, pp. 477 ff.

[20] It should be kept in mind here that (5.1), (5.2), (5.5), (5.6) are derived under the assumption that the volume G tends to infinity at fixed H', i.e., that

$$(e/c)H' \gg (2mkT)^{\frac{1}{2}}/R \ (A),$$

where R is the radius of the cylindrical container. The above statement therefore holds only for fields fulfilling (A), and "arbitrarily small fields" strictly means "fields of the order $(2mkT)^{\frac{1}{2}}/R$."

where H is the applied field, $M=-\partial\Omega(H')/\partial H'$ the magnetization, cannot be applied here. In fact, an estimate (see Appendix II) shows that for all values of H' which need be considered, the diameter of the bosons' orbits are much larger than the mean distance between particles, provided that the right-hand side of (3.3) is small, i.e., provided that

$$\eta\equiv(e^2/mc^2)n^{\frac{1}{3}}\ll 1. \tag{5.9}$$

The field produced by any one such large orbit is negligible compared to the average field, and, therefore, the "acting" field H' has to be identified with the average microscopic field B.[21]

$$H'=B=H+4\pi M \tag{5.10}$$

It will be shown at the end of this section that, apart from negligible corrections, for $T<T_c(1-\eta)$:

$$\begin{aligned}M(H')&=-n_s\mu_0\frac{H'}{|H'|}\\&=-n\mu_0\frac{H'}{|H'|}\left[1-\left(\frac{T}{T_c}\right)^{\frac{3}{2}}\right],\end{aligned} \tag{5.11}$$

where μ_0 is the Bohr magneton. In a magnetic field B, therefore, the Bose gas exhibits a permanent diamagnetic moment, it is a "dia-ferromagnet." No condensed phase exists.

From (5.10) and (5.11), it can be seen that the $B(H)$-curve for the Bose-gas is given by

$$B(H)=\begin{cases}0 & H<H_0\\ H-H_0 & H>H_0\end{cases}, \tag{5.12}$$

with

$$H_0=4\pi n\mu_0[1-(T/T_c)^{\frac{3}{2}}]. \tag{5.13}$$

This means that for $H>H_0$ a field H applied to the surface of the cylinder penetrates the Bose gas as a *homogeneous* field, producing a magnetization M and an induction B related by (5.10) and (5.11). For $H<H_0$, however, no *homogeneous* field can penetrate the Bose gas; indeed, assuming a homogeneous $H<H_0$ leads to a contradiction in (5.10) and (5.11). If one applies to the surface of the cylinder an $H<H_0$ the bosons condense, expel the field except for a thin surface layer—inhomogeneous fields are, of course, outside the scope of the approach in this section—and the superconducting state is established. $H_0(T)$ (5.12) is, therefore, the critical field. Using (3.6) and (3.7), $H_0(T)$ can be related to the penetration depth d:

$$H_c=\hbar c/2ed^2. \tag{5.14}$$

The $B(H)$ law (5.12) of the Bose gas differs from the one usually assumed for superconductors,[22] and therefore the thermodynamical relations have to be reinvestigated.

Calling $\Phi(T)$ the free energy of the Bose gas at vanishing field, the thermodynamical potential with variables T and H, $G(H,T)$,[23] is given by

$$G(H,T)=\Phi(T)-\frac{1}{4\pi}\int_0^H BdH$$

and hence

$$\begin{aligned}&G_s(H,T)=\Phi(T);\quad (H<H_0),\\&G_n(H,T)=\Phi(T)-(1/8\pi)(H-H_0)^2;\quad (H>H_0).\end{aligned} \tag{5.15}$$

From this, one finds for the latent heat of the transition in the field

$$Q=-T\frac{\partial}{\partial T}(G_n-G_s)_{H=H_0}=\frac{1}{8\pi}T\frac{\partial(H-H_0)^2}{\partial T}\bigg|_{H=H_0}. \tag{5.16}$$

The jump in the specific heat is, similarly

$$\begin{aligned}C_n-C_s&=-T\frac{\partial^2}{\partial T^2}(G_n-G_s)_{H=H_0}\\&=\frac{T}{8\pi}\frac{\partial^2}{\partial T^2}(H-H_0)^2|_{H=H_0},\end{aligned} \tag{5.17}$$

or

$$C_n-C_s=\frac{T}{8\pi}\left(\frac{\partial H_0}{\partial T}\right)^2.$$

One sees that the thermodynamic properties of the ideal Bose gas are not in agreement with the properties of actual superconductors. The transition in the magnetic field is still of the second kind, having no latent heat; however, a jump in the specific heat occurs for $H\neq 0$.[24]

There now remains to calculate $M(H')$ from the basic equations (5.5) and (5.6). We shall do this separately for the absolute zero and for higher temperatures.

(a) *Absolute Zero:* $\mu_0 B\gg kT$

Here, (5.5) and (5.6) reduce to

$$\omega=-n\mu_0 H'\left(\frac{T}{T_c}\right)^{\frac{3}{2}}\frac{2}{\zeta(\frac{3}{2})}\sum_{\nu=1}^{\infty}\frac{\exp[-\alpha(\mu_0H'-\mu)\nu]}{\nu^{\frac{3}{2}}}, \tag{5.18}$$

$$n=n\left(\frac{T}{T_c}\right)^{\frac{3}{2}}\frac{2}{\zeta(\frac{3}{2})}\alpha\mu_0H'\sum_{\nu=1}^{\infty}\frac{\exp[-\alpha(\mu_0H'-\mu)\nu]}{\nu^{\frac{1}{2}}}, \tag{5.19}$$

[21] From (5.10) one can deduce the following relation between the susceptibility χ and the quantity χ' of (1.5):

$$\chi=\chi'/(1-4\pi\chi').$$

This shows that on approaching condensation, where $\chi'\to-\infty$, $\chi\to-1/4\pi$ so that the permeability tends to zero, in accordance with (5.12). See also H. Fröhlich, Nature **168**, 280 (1951).

[22] C. J. Gorter and H. B. G. Casimir, Physica **1**, 305 (1934).

[23] See reference 9, paragraph 2.

[24] It should be borne in mind that (5.11) and all subsequent equations become invalid near the transition temperature. It follows from (5.17) that $H_0(T)$ must have a vanishing derivative at $T=T_c$, since there $C_n=C_s=0$.

where use has been made of the equation valid for $T<T_c$.

$$n_0=n(T/T_c)^{\frac{3}{2}}, \tag{5.20}$$

The factor $(T/T_c)^{\frac{3}{2}}\alpha\mu_0 H$ tends to zero as $T\to 0$, and therefore the sum in (5.19) must tend to infinity as $T\to 0$, i.e.,

$$\alpha(\mu_0 H'-\mu)\to 0 \quad \text{as} \quad T\to 0.$$

At $T=0$ therefore, one has

$$\mu=\mu_0 H',$$

$$\omega=0,$$

and thus the free energy per unit volume is

$$\varphi(H',0)\equiv\omega+\mu n=n\mu_0 H'. \tag{5.21}$$

The magnetization is

$$M=-\partial\varphi/\partial H'=-n\mu_0. \tag{5.22}$$

It is of no great use to make an expansion in powers of temperature starting from (5.18) and (5.19), because the range of validity of such an expansion is limited to a very small interval, *viz.:*

$$T/T_c\ll\eta'\equiv 4\pi n\mu_0^2/kT_c, \tag{5.23}$$

and this latter ratio is of the same order of magnitude as η (5.9) and thus very small for all reasonable values of e, m, n.

(b) Finite Temperatures: $\mu_0 H\ll kT$

For $\alpha\mu_0 H\ll 1$, it is shown in Appendix III that the expressions (5.5) and (5.6) can be transformed into

$$n-n_0=n_0\frac{2\sqrt{\pi}}{\zeta(\frac{3}{2})}(\alpha\mu_0 H')^{\frac{1}{2}}F(s), \tag{5.22}$$

$$\omega+\mu n-\omega_0=n_0\frac{2\sqrt{\pi}}{\zeta(\frac{3}{2})}kT(\alpha\mu_0 H')^{\frac{3}{2}}\Phi(s), \tag{5.23}$$

where n_0 is given by (5.7), ω_0 by (5.5) with $H'=0$, $\mu=0$, $s=1-\mu/(\mu_0 H')$,

$$\Phi(s)=\pi^{-1}G(s)+(1-s)F(s), \tag{5.24}$$

and

$$F(s)=\sum_{n=1}^{\infty}\frac{\cos[\pi(ns-\frac{1}{4})]}{n^{\frac{1}{2}}},$$
$$G(s)=\sum_{n=1}^{\infty}\frac{\sin[\pi(ns-\frac{1}{4})]}{n^{\frac{3}{2}}}. \tag{5.25}$$

An expansion of these functions for small $|s|$ can be obtained by using the well-known expansion[25]

$$Z_\alpha(x)\equiv\sum_{\nu=1}^{\infty}\frac{e^{-x\nu}}{\nu^\alpha}=\frac{\pi}{\sin\pi\alpha}\frac{x^{\alpha-1}}{\Gamma(\alpha)}+\sum_{\lambda=0}^{\infty}\frac{(-1)^\lambda}{\lambda!}\zeta(\alpha-\lambda)x^\lambda \tag{5.26}$$

[25] J. E. Robinson, Phys. Rev. **83**, 678 (1951); M. R. Schafroth, Proc. Phys. Soc. (London) **A67**, 33 (1953); J. Clunie, Proc. Phys. Soc. (London) **A67**, 682 (1954).

valid for nonintegral α, $\mathrm{Re}(x)>0$, and $|x|<2\pi$. One finds

$$F(s)=s^{-\frac{1}{2}}+\frac{\zeta(\frac{1}{2})}{\sqrt{2}}+\frac{\pi\zeta(-\frac{1}{2})}{\sqrt{2}}s+O(s^2),$$
$$G(s)=-\frac{\zeta(\frac{3}{2})}{\sqrt{2}}+2\pi s^{\frac{1}{2}}+\frac{\pi\zeta(\frac{1}{2})}{\sqrt{2}}s+O(s^2). \tag{5.27}$$

Introducing the dimensionless variables

$$h=H'/4\pi n\mu_0^2, \quad t=T/T_c$$

(5.24) and (5.25) read

$$1=\frac{2\sqrt{\pi}}{\zeta(\frac{3}{2})}\frac{t}{1-t^{\frac{3}{2}}}(h\eta')^{\frac{1}{2}}F(s), \tag{5.30}$$

$$\frac{\varphi(H',T)-\varphi(0,T)}{4\pi n^2\mu_0^2}=\frac{2\sqrt{\pi}}{\zeta(\frac{3}{2})}t(\eta')^{\frac{1}{2}}h^{\frac{3}{2}}\Phi(s). \tag{5.31}$$

From (5.30) it follows that for $\eta'^{\frac{1}{2}}\ll 1-t^{\frac{3}{2}}$ we can restrict ourselves to the first terms in the expansion (5.29), so that $\Phi(s)\approx F(s)$. Then, (5.31) yields

$$\varphi(H',T)-\varphi(0,T)=4\pi n^2\mu_0^2(1-t^{\frac{3}{2}})h=n\mu_0(1-t^{\frac{3}{2}})H', \tag{5.32}$$

and

$$M(H',T)\equiv-\frac{\partial\varphi(H',T)}{\partial H'}=-n\mu_0(1-t^{\frac{3}{2}}),$$
$$M(H',T)=-n_s\mu_0, \tag{5.33}$$

which proves our earlier statement. (5.33) is valid as long as

$$1-(T/T_c)^{\frac{3}{2}}\gg(\eta')^{\frac{1}{2}}. \tag{5.34}$$

6. CONCLUSION AND OUTLOOK

As shown in the preceding sections, an ideal gas of charged bosons at low temperatures exhibits qualitatively the same magnetic and thermodynamic properties as a superconductor. The only differences are the continuity of the specific heat through the transition point and the form of the $B(H)$ curve. The nonequilibrium properties (e.g., the vanishing of electrical resistance) are clearly outside the scope of the model, since it does not provide any mechanism for electrical resistance even above the transition temperature.

In view of the fact that the Bose gas is the only known system with superconducting properties, it is tempting to assume that the occurrence of superconductivity in metals is due to the formation of some kind of charged bosons at low temperatures. Without prejudicing the nature of these bosons, one may get some insight about them by trying to fit experimental data to the ideal-gas model.

The model contains three parameters, the mass m, the charge e and the density n of the bosons. These can be fitted to three experimental data: the transition temperature T_c, the penetration depth d_0 at $T=0$, and the critical field $H_c(0)$ at $T=0$. If one tries this, one gets utterly implausible results ($n\approx 10^{17}$ cm^{-3}, $m\approx 10^8$ electron masses). Only the charge falls into the reasonable order of magnitude of a few elementary charges. This fact may give a clue for the understanding of the actual situation if one notices that the charge is determined through (5.14) by $H_c(0)$ and d_0 alone, i.e., by two quantities at zero temperature, whereas m and n require comparison of properties at $T=0$ and $T=T_c$. It seems, therefore, that one will have to consider a creation of more bosons with decreasing temperature. If one allows for this and assumes a reasonable boson mass of the order of the electron mass, one can compute the density n of bosons at $T=T_c$ from (1.1) and at $T=0$ from (3.7), and one finds

$$n(T)_c\approx 10^{17}\ \text{cm}^{-3},$$
$$n(0)\approx 10^{22}\ \text{cm}^{-3},$$

i.e., a considerable increase. On the other hand, this picture does not affect the relation (5.14) between $H_c(0)$ and d_0 which shows that the charge of the bosons is of the order of a few electron charges e_0. For tin, e.g., taking $d_0=5.2\times 10^{-6}$ cm and $H_c(0)=300$ gauss one gets $e=4e_0$.

This picture has the further consequence that η' (5.23) and η (5.9) are no longer of the same order of magnitude, since the former now involves $n(0)/[n(T_c)]^{\frac{2}{3}}$, and the latter $[n(T_c)]^{\frac{1}{3}}$. The temperature interval in which $K_n(q^2)$ is important and (5.11) fails, thus remains small $((T_c-T)/T_c\gg 10^{-7})$, whereas $\eta'=\mu_0 H_c(0)/kT_c \sim 10^{-2}$.

It is also interesting to note that the relation (5.14), as a function of temperature, holds approximately in actual superconductors, the product of d^2H_0 varying only by about 50% over the range $0<T<T_c$, whereas the temperature dependence (3.6) of d alone is quite different from the one in superconducting metals. This seems to corroborate the assumption that actual superconductivity is related to the properties of a Bose gas whose total particle number depends on temperature.

A theoretical picture which accounts for a temperature-dependent density of bosons has been proposed by the author[11] on the assumption that the bosons are resonant two-electron states. However, a rough treatment which neglected the width of the resonance altogether was not sufficient to fit the facts quantitatively, mainly because the increase in the density of bosons between the transition point and absolute zero could not be made large enough. It is, however, expected that a more refined elaboration of the same picture would lead to appreciable improvement.

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APPENDIX I. EXPANSION OF $k(z)$

We wish to expand

$$k_\epsilon(z)=\int_0^\infty dx\left[\frac{x}{2z}(x^2-z^2)\times\log\left|\frac{x-z}{x+z}\right|+x^2\right]\frac{1}{\exp(x^2+\epsilon)-1} \tag{I.1}$$

in powers of z in the limit $\epsilon\to 0$. First we notice that the integrand is even in x, so that

$$k_\epsilon(z)=\tfrac{1}{2}\int_{-\infty}^{+\infty} dx\left[\frac{x}{2z}(x^2-z^2)\times\log\left|\frac{x-z}{x+z}\right|+x^2\right]\frac{1}{\exp(x^2+\epsilon)-1}. \tag{I.1'}$$

This can be expressed in the complex x-plane, with a cut from $-z$ to $+z$, in which $\log(x-z)$ is real for real $x-z>0$.

$$k_\epsilon(z)=\tfrac{1}{2}\ \mathrm{Re}\int_C dx\left[\frac{x}{2z}(x^2-z^2)\times\log\left(\frac{x-z}{x+z}\right)+x^2\right]\frac{1}{\exp(x^2+\epsilon)-1} \tag{I.2}$$

where Re denotes "real part" and C is the path shown in Fig. 1. (2) can then be reduced to an integral over a path C' on which everywhere $|x|>z$ and a residue at the pole $x_0=+i\epsilon^{\frac{1}{2}}$.

The residue contributes

$$R(\epsilon,z)\equiv\tfrac{1}{2}\ \mathrm{Re}\left\{2\pi i \operatorname*{residue}_{x=x_0}\left(\left[\frac{x}{2z}(x^2-z^2)\times\log\left(\frac{x-z}{x+z}\right)+x^2\right)\frac{1}{\exp(x^2+\epsilon)-1}\right\}$$
$$=+\pi\ \mathrm{Re}\left\{i\left[\frac{i\epsilon^{\frac{1}{2}}}{2z}(-\epsilon-z^2)\times\log\left(\frac{i\epsilon^{\frac{1}{2}}-z}{i\epsilon^{\frac{1}{2}}+z}\right)-\epsilon\right]\frac{1}{2i\epsilon^{\frac{1}{2}}}\right\}. \tag{I.3}$$

In the limit $\epsilon\to 0$, we have

$$\log\left(\frac{i\epsilon^{\frac{1}{2}}-z}{i\epsilon^{\frac{1}{2}}+z}\right)\to i\pi,$$

and thus

$$R(0,z)=(\pi^2/4)z. \tag{I.4}$$

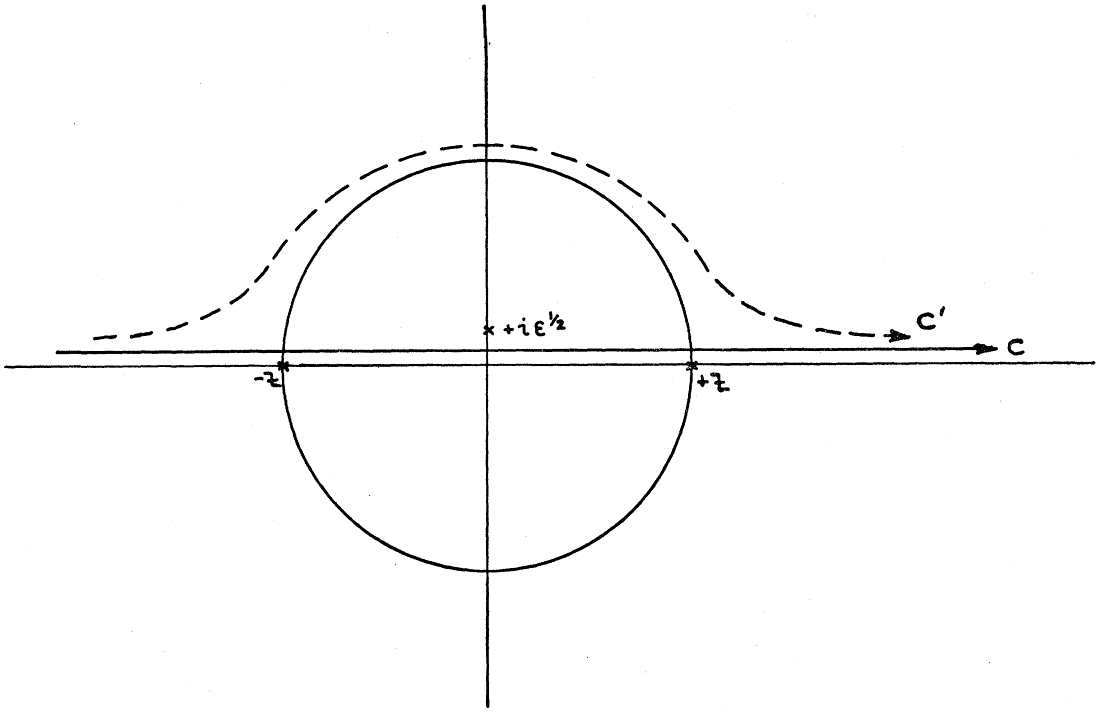

FIG. 1. Paths in the complex x-plane.

We therefore get

$$k_0(z)=\frac{\pi^2}{4}z+\tfrac{1}{2}\,\mathrm{Re}\int_{C'} dx\left[\frac{x}{2z}(x^2-z^2)\times\log\left(\frac{x-z}{x+z}\right)+x^2\right]\frac{1}{\exp(x^2)-1}. \tag{I.5}$$

In the remaining integral, $|z|<|x|$, so that we can expand the expression in brackets in powers of z/x. The first term is easily calculated to be

$$\left[\frac{x}{2z}(x^2-z^2)\log\left(\frac{x-z}{x+z}\right)+x^2\right]=\tfrac{2}{3}z^2+O(z^4), \tag{I.6}$$

so that

$$k_0(z)=\frac{\pi^2}{4}z+\frac{z^2}{3}\,\mathrm{Re}\int_{C'} dx\frac{1}{\exp(x^2)-1}. \tag{I.7}$$

The remaining z-independent integral can be reduced by the substitution $x^2=t$, to the well-known integral representation of Riemann's zeta function[26] $\zeta(s)$ for $s=\frac{1}{2}$ and we finally get

$$k_0(z)=\frac{\pi^2}{4}z+\frac{\sqrt{\pi}}{3}\zeta(\tfrac{1}{2})z^2+O(z^4), \tag{I.8}$$

which is the result (2.29).

[26] E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, Cambridge, 1946), fourth edition, p. 266.

APPENDIX II. ESTIMATE OF RADII OF ORBITS IN MAGNETIC FIELD

The radius of the classical orbit of a particle moving with energy E in a field H' is given by

$$\rho=(c/eH')(2mE)^{\frac{1}{2}}. \tag{II.1}$$

As long as $\mu_0H'\ll kT$, we may replace E by the average kinetic energy of a free particle, i.e.,

$$(2mE)^{\frac{1}{2}}\approx\frac{1}{n}\frac{m^2}{\pi^2\hbar^3}(kT)^2\zeta(2). \tag{II.2}$$

The maximum value for H' we need is

$$H_0(0)=4\pi n\mu_0. \tag{II.3}$$

Therefore

$$\frac{\rho}{a}\geq\mathrm{const}\frac{a}{r_0}\left(\frac{T}{T_c}\right)^2=\frac{\mathrm{const}}{\eta}\left(\frac{T}{T_c}\right)^2, \tag{II.4}$$

where $r_0=e^2/mc^2$, $a=n^{-\frac{1}{3}}=$ mean distance between particles.

This estimate breaks down near $T=0$. Here we have to assume $\mu_0H'\gg kT$, and to take for E the ground-state energy of a particle in a magnetic field:

$$E\approx\mu_0H', \tag{II.5}$$

(II.1) then yields

$$\rho\geq d_0\gg a, \tag{II.6}$$

where d_0 is the penetration depth at absolute zero, (5.7).

(II.4) and (II.6) establish the required estimate

$$\rho/a \gg 1 \tag{II.7}$$

for the whole range of temperature and fields of interest.

APPENDIX III. REDUCTION OF (5.5) AND (5.6) TO (5.24) AND (5.25)

In the case of $\alpha\mu_0 H' \ll 1$, it is convenient to consider instead of ω and n the following linear combinations

$$\zeta(\tfrac{3}{2})\frac{n_0-n}{n_0} \equiv A = \sum_{\nu=1}^{\infty}\frac{1}{\nu^{\frac{3}{2}}}\left[1-e^{\alpha\mu\nu}\frac{x\nu}{\sinh(x\nu)}\right], \tag{III.1}$$

$$\alpha\zeta(\tfrac{3}{2})\frac{\omega+\mu n-\omega_0}{n_0} \equiv B = \sum_{\nu=1}^{\infty}\frac{1}{\nu^{5/2}} \times\left[1-e^{\alpha\mu\nu}\frac{x\nu}{\sinh(x\nu)}(1-\alpha\mu\nu)\right], \tag{III.2}$$

with $x \equiv \alpha\mu_0 H' \ll 1$. These are the physical quantities actually required and are also mathematically convenient for the following reason: Due to our assumption $x \ll 1$ and the ensuing one $\alpha\mu \ll 1$ (in view of $0<\mu<\mu_0 H'$), we can replace the sums over ν by integrals, provided these converge at the lower limit. The combinations (III.1) and (III.2) are just such that this holds, and we therefore write

$$A = \int_0^\infty \frac{d\nu}{\nu^{\frac{3}{2}}}\left[1-e^{\alpha\mu\nu}\frac{x\nu}{\sinh(x\nu)}\right], \tag{III.3}$$

$$B = \int_0^\infty \frac{d\nu}{\nu^{5/2}}\left[1-e^{\alpha\mu\nu}\frac{x\nu}{\sinh(x\nu)}(1-\alpha\mu\nu)\right]. \tag{III.4}$$

These integrals can be evaluated by expanding their integrands into partial fractions, using the theorem of Mittag-Leffler. One finds that

$$\frac{1}{\nu}\left[1-e^{\alpha\mu\nu}\frac{x\nu}{\sinh(x\nu)}\right] = \sum_{n=1}^{\infty}(-1)^{n-1}\left\{\frac{\exp\left(i\pi n\frac{\alpha\mu}{x}\right)}{\nu-\frac{i\pi n}{x}} + \frac{\exp\left(-i\pi n\frac{\alpha\mu}{x}\right)}{\nu+\frac{i\pi n}{x}}\right\}, \tag{III.5}$$

$$\frac{1}{\nu^2}\left[1-e^{\alpha\mu\nu}\frac{x\nu}{\sinh(x\nu)}(1-\alpha\mu\nu)\right] = \sum_{n=1}^{\infty}(-1)^{n-1}\left\{\frac{x}{n\pi i}\left(1-in\pi\frac{\alpha\mu}{x}\right)\frac{\exp\left(i\pi n\frac{\alpha\mu}{x}\right)}{\nu-\frac{i\pi n}{x}} - \frac{x}{n\pi i}\left(1+in\pi\frac{\alpha\mu}{x}\right)\frac{\exp\left(-i\pi n\frac{\alpha\mu}{x}\right)}{\nu+\frac{i\pi n}{x}}\right\}. \tag{III.6}$$

The integration in A and B then gives

$$A = 2(\pi x)^{\frac{1}{2}}\sum_{n=1}^{\infty}\frac{(-1)^{n-1}}{n^{\frac{1}{2}}}\cos\left[\pi\left(n\frac{\alpha\mu}{x}+\tfrac{1}{4}\right)\right], \tag{III.7}$$

$$B = \frac{2}{\sqrt{\pi}}x^{\frac{3}{2}}\sum_{n=1}^{\infty}\frac{(-1)^{n-1}}{n^{\frac{3}{2}}}\sin\left[\pi\left(n\frac{\alpha\mu}{x}+\tfrac{1}{4}\right)\right] - 2(\pi x)^{\frac{1}{2}}\alpha\mu\sum_{n=1}^{\infty}\frac{(-1)^{n-1}}{n^{\frac{1}{2}}}\cos\left[\pi\left(n\frac{\alpha\mu}{x}+\tfrac{1}{4}\right)\right]. \tag{III.8}$$

Putting $s = 1-\alpha\mu/x = 1-\mu/(\mu_0 H')$ these expressions become

$$A = -2\sqrt{\pi}(\alpha\mu_0 H')^{\frac{1}{2}}\sum_{n=1}^{\infty}\frac{1}{n^{\frac{1}{2}}}\cos[\pi(ns-\tfrac{1}{4})] = -2\sqrt{\pi}(\alpha\mu_0 H')^{\frac{1}{2}}F(s). \tag{III.9}$$

$$B = \frac{2}{\sqrt{\pi}}(\alpha\mu_0 H')^{\frac{3}{2}}\sum_{n=1}^{\infty}\frac{1}{n^{\frac{3}{2}}}\sin[\pi(ns-\tfrac{1}{4})] + 2(\pi)^{\frac{1}{2}}(\alpha\mu_0 H')^{\frac{1}{2}}\alpha\mu\sum_{n=1}^{\infty}\frac{1}{n^{\frac{1}{2}}}\cos[\pi(ns-\tfrac{1}{4})] = \frac{2}{\sqrt{\pi}}(\alpha\mu_0 H')^{\frac{3}{2}}\{G(s)+\pi(1-s)F(s)\}, \tag{III.10}$$

with $F(s)$ and $G(s)$ defined by (5.27). Inserting (III.9) and (III.10) into (III.1) and (III.2) readily gives (5.24) and (5.25).