PREPRINT N.801
10 Maggio 1991

Dipartimento di Fisica
Università di Roma "La Sapienza"

AN INTRODUCTION TO SUPERCONDUCTIVITY

C.DiCastro, R. Raimondi

Dipartimento di Fisica, Università degli studi di Roma "La Sapienza" I-00185 Roma, Italy

1 PREFACE

According to the request of the organizers of this school, these lecture notes have been designed as an introductory course to ordinary superconductivity given by one of us (CDC).

Few basic concepts like ordering and its consequences have been the guiding ideas. The specific order (pair condensation) occuring in superconductivity and the related order parameter have been shown to give rise to all the super effects via the Landau-Ginzburg formulation of the Landau theory of the second order phase transitions.

The condensation criterion for interacting fermions finds its simple formulation within the density matrix approach. The concept of off-diagonal long range order (ODLRO) of the two particle reduced density matrix defines naturally the order parameter for superconductivity.

The anomalous factorization property of the two particle reduced density matrix associated to ODLRO gives rise to a generalized Hartree-Fock formulation of the Bardeen Cooper and Schrieffer theory. The same approach allows for a simple derivation of the time dependent Landau-Ginzburg equation for the order parameter. The density matrix approach becomes then the bridging formalism between the phenomenology and the microscopic theory.

No high T_c superconductivity will be here considered except for few comments when we study the limits of validity of the mean field approximation, the order parameter fluctuations and their precursor effects.

2 PHENOMENOLOGY OF SUPERCONDUCTORS: LONDON THEORY AND LANDAU CRITERION

In this section we shall briefly recall those experimental aspects of ordinary superconductors [1] which we believe are important to the discussion of the basic concepts of the theory. We shall also point out some phenomenological interpretations of these experimental facts.

Many metals and alloys below their superconductive transition temperature T_c have a stable flux of charge carriers also in the absence of an external driving field, i.e. the resistivity approaches zero at the transition. The possibility of having persistent currents is not true for any magnitude of the current. There exists a critical value of the current above which the superconductivity disappears. Related to this critical current there is a critical magnetic field which goes to zero at T_c as

$$H_c(T) = H_0(1 - (T/T_c)^2) \tag{2.1}$$

with H_0 of the order of $10^2 G$. The slope of the separation curve at T_c is finite and negative. For ordinary superconductors T_c is of the order of few Kelvin and usually has a crystal ionic mass dependence $T_c \sim M^{1/2}$ (isotope effect).

Infinite conductivity implies that inside a superconductor $\mathbf{E} = 0$ and due to the Maxwell equation

$$rot\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t} \tag{2.2}$$

the magnetic induction B is constant. This constancy of B would induce a dependence of the final superconductive state in the presence of a magnetic field on the history of how this state has been achieved i.e. if the external magnetic field is varied before or after reducing the temperature below T_c. Superconductors however exhibit the Meissner-Ochsenfeld effect: the magnetic field is expelled from the bulk of a superconductive sample,thus imposing always $B = 0$ in the final superconductive state. Actually B and E are vanishing everywhere but in a thin layer of depth

λ at the surface. λ is temperature dependent and goes to infinity at the critical temperature

$$\lambda = \lambda_0[1 - (T/T_c)^4]^{-1/2}; \quad \lambda \sim (\lambda_0/2)[1 - T/T_c]^{-1/2} \; for \; T \rightarrow T_c. \tag{2.3}$$

Its zero temperature value λ_0 is of the order of a few hundred Angstrom. The phenomenological conditions for superconductivity are therefore the conductivity $\sigma \rightarrow \infty$ and $B = 0$.

Along the phase boundary between the normal and the superconducting phase, the continuity of the Gibbs free energy implies the analogue of the Clausius-Clapeyron equation

$$\frac{dH_c(T)}{dT} = \frac{S_n - S_s}{M_s - M_n} \tag{2.4}$$

where S_n,S_s,M_n, M_s are the entropies and magnetizations per unit volume for normal and superconducting state respectively. For the normal state we can put $M_n \sim 0$ and because of the Meissner-Ochsensfeld effect, $M_s = -(H/4\pi)$; the entropy difference between the normal and the superconducting state is then given by

$$S_n - S_s = -\frac{1}{4\pi} H_c \frac{dH_c}{dT} \tag{2.5}$$

$S_n - S_s$ is positive for any $T < T_c$, except at T_c where the transition is of second order. The superconducting phase is more ordered, although X-ray experiments show no structural modifications of the conduction electrons.

The specific heat of a superconductor has two peculiarities: i) It is discontinous at the transition from normal to superconducting phase [2].

ii)At low temperatures it goes to zero exponentially [3], in contrast to the linear T behavior of ordinary metals.

The jump ΔC in the specific heat is accounted for by taking the derivative with respect to the temperature of the entropy difference of eq.(2.4) and is given by $\Delta C = \frac{T_c}{4\pi}(dH_c/dT)^2|_{T=T_c} > 0$. The discontinuity in the specific heat is a common feature of the second order phase transitions when treated in mean field approximation.

The low temperature exponential decrease of the specific heat gives evidence for the existence of a temperature dependent gap $\Delta(T)$ in the excitation spectrum as shown also by infrared transmission and reflection measurements [4] and by tunneling experiments [5]. Near T_c, $\Delta(T)$ behaves as

$$\Delta \sim (1 - T/T_c)^{1/2} \tag{2.6}$$

The second order phase transitions are characterised by the existence of an order parameter ψ specifying the amount of ordering in the low temperature phase, which goes to zero at the critical point. Within the mean field approximation the order parameter goes to zero as the square root of the deviation from the critical temperature, thus suggesting that Δ is related to the order parameter of the superconductive transition, which seems to be well described in the mean field approximation.

The phenomenological theory proposed by the brothers F. and H. London [6] rationalizes the problems arisen by the above listed experimental facts.

The first observation concerns the consequences we can deduce for a system which has infinite conductivity . If we call $\mathbf{v}_s$ the velocity of the charge carriers in the absence of dissipation, the equation of motion can be written as

$$m\frac{d\mathbf{v}_s}{dt} = -e^*\mathbf{E}$$

where e^* is the effective charge. We have assumed here that the carriers have negative charge having in mind that in metals the electrons are responsible for the electrical transport. Combining this equation with eq.(2.2) we get

$$\frac{d}{dt}\left(rot\mathbf{J}_s + \frac{n_s e^{*2}}{mc}\mathbf{B}\right) = 0. \tag{2.7}$$

Here we have introduced the supercurrent $\mathbf{J}_s = -e^* n_s \mathbf{v}_s$, n_s being the carrier density. Every static field $\mathbf{B}$ satisfies the above equation. Inside a superconductor moreover $\mathbf{B} = 0$. London showed that this last condition is obtained by introducing the additional equation

$$rot\mathbf{J}_s + \frac{n_s e^{*2}}{mc}\mathbf{B} = 0 \tag{2.8}$$

In fact substituting now in the eq.(2.8) the expression for the current given by the Maxwell equation $\mathbf{J} = c/4\pi rot\mathbf{B}$, we obtain

$$\nabla^2\mathbf{B} = \lambda^{-2}\mathbf{B} \qquad \lambda^2 = \frac{mc^2}{4\pi n_s e^{*2}}. \tag{2.9}$$

It is easy to show that for a bulk superconductor occupying the half space $x > 0$, eq.(2.9) implies for the magnetic induction $\mathbf{B}$ exponentially decreasing solutions of the form

$$\mathbf{B}(x) = \mathbf{B}(0)e^{-x/\lambda}$$

and the Meissner effect follows. Here the length λ is called the London penetration depth and gives a measure of n_s. From the temperature dependence of λ near T_c given by eq.(2.3), we deduce now that n_s should behave as the square of Δ i.e. as the square of the order parameter. This consideration will be important in building up a theory of superconductivity.

A local relation between the current and the field has been implicitly assumed in the London equation. In fact if we choose the London gauge for the vector potential $div\mathbf{A} = 0$, $A_\nu = 0$ (A_ν being the component of $\mathbf{A}$ perpendicular to the boundary surface) and consider an isolated simply connected superconductor ($div\mathbf{J} = 0$) eq.(2.8) implies

$$\mathbf{J}_s = -\frac{c}{4\pi\lambda^2}\mathbf{A}. \tag{2.10}$$

In general, as was first indicated by Pippard [7] and successively shown by the microscopic theory, the current depends on the vector potential through a non local relation

$$\mathbf{J}(\mathbf{r}) = \int d\mathbf{r}' K(\mathbf{r}, \mathbf{r}')\mathbf{A}(\mathbf{r}').$$

The typical distance over which $\mathbf{A}$ and $\mathbf{J}$ vary is given by the London penetration depth λ, while the kernel K varies over a characteristic distance ξ_0, which from dimensional analysis is of the order of $\xi_0^{-1} \sim k_B T/\hbar v_F$.

The superconductors for which $\xi_0 > \lambda$ are named Pippard or type I superconductors, while those for which $\xi_0 < \lambda$ are named London or type II superconductors.

A complete diamagnetism is shown for type I superconductors only. For type II superconductors the penetration of the field starts at the critical field $H_{c_1}(T)$ less than the thermodynamic critical field $H_c(T)$ and is completed at an upper critical field $H_{c_2}(T)$ larger than $H_c(T)$.

The London equation has a very deep meaning. We recall that in the presence of a static vector potential the momentum of a particle is expressed as $\mathbf{p} = m\mathbf{v} + \frac{e^*}{c}\mathbf{A}$. Eq.(2.10) implies that the carriers responsible for superconductivity are in a state of zero momentum

$$\mathbf{p} = \frac{e^*}{c}\left(\frac{mc}{n_s e^{*2}}\mathbf{J}_s + \mathbf{A}\right) = 0. \qquad (2.11)$$

In the ordinary metals in the absence of a scalar field we have instead $\mathbf{J} = 0$ and $\mathbf{p}$ varies with $\mathbf{A}$ from point to point.

The above phenomenological analysis shows that the transition from normal to superconducting state is an ordering transition. The London theory implies that this ordering occurs in momentum space. The ordering specifies the nature of the phase transition but has not direct implications on the stability of the flux which is a prerequisite for superconductivity and superfluidity in general. Before going to discuss how condensation in momentum space is possible for a Fermi system and give a general criterion for it , we therefore discuss the general criterion for superfluidity due to Landau [8].

The argument proposed by Landau is concise and very general. Let us consider a moving fluid in a capillary. The viscosity manifests itself with the loss of the total kinetic energy of the fluid and the appearance of inner collective motions. These collective motions are described in terms of elementary excitations and are characterized by a well defined dispersion law. On the assumption that the fluid can interact with an external body (the wall) through the creation or annihilation of elementary excitations only, in a frame moving with the fluid at velocity $\mathbf{v}$, the total energy and momentum are those of the elementary excitations. Instead, in a frame at rest with respect to the fluid, in the presence of a single excitation $\epsilon(\mathbf{p})$ the energy and momentum are, according to the Galileian transformations,

$$E = \epsilon(\mathbf{p}) + \mathbf{p}\cdot\mathbf{v} + \frac{1}{2}Mv^2 \tag{2.12}$$

$$\mathbf{P} = \mathbf{p} + M\mathbf{v} \tag{2.13}$$

where M is the total mass of the fluid. The condition for the creation of a single excitation and the appearance of viscosity is $\Delta\vec{E} = \epsilon(\mathbf{p}) + \mathbf{p}\cdot\mathbf{v} < 0$, which means

$$v > \frac{\epsilon(p)}{p}\Big|_{min} \equiv v_c. \tag{2.14}$$

On the above assumption in order to have viscosity the velocity must be greater than a critical value, which depends on the excitation spectrum of the system.

We note that the Landau criterion tells us that the Bose gas cannot be a superfluid. In fact the free-like spectrum of a Bose gas has $v_c = 0$. The λ superfluid transition of Helium (^4He) cannot be simply modelled with a Bose gas eventhough the Bose-Einstein condensation is relevant for its interpretation.

The linear phonon spectrum at low wave vector **k** and the roton excitations with gap at high **k** values for the real superfluid Helium [9] satisfiy the Landau criterion with a finite value v_c. In real superconductors the existence of a gap in the low lying excitations provides the required stability of the flux.

3 THE CONDENSATION CRITERION AND THE ORDER PARAMETER

As we have seen in the previous section two requirements have to be satisfied by any theory of superconductivity:

1.The Landau criterion, which is related to the stability of the flux and gives a condition to be imposed on the excitation spectrum of the system.

2.The superconductive phase is highly ordered, and the ordering occurs in momentum space.

Each condition by itself is not sufficient to describe superconductors. The first does not say what kind of transition the system undergoes at the critical temperature. The second one does not ensure superfluidity. There is no explicit connection between the two conditions; however every explicit model of superconductivity or superfluidity satisfying one of them satisfies the other.

A general criterion for condensation [10, 11] has been formulated. We discuss first a system of bosons which is relevant for studying the superfluidity of ^4He. We shall afterwards show which modifications are to be made for a system of fermions. In this latter case the condensation criterion itself will give us hints on what kind of microscopic theory we have to build.

In the case of a Bose gas we speak of Bose-Einstein condensation when in the thermodynamic limit a finite fraction of the total number of particles are in the zero momentum state

$$\lim_{N,\Omega\to\infty,\frac{N}{\Omega}=const} \frac{n_0}{N} = 1-(T/T_c)^{3/2} \quad T \leq T_c$$

$$\frac{n_0}{N} = 0 \quad T > T_c.$$

Such a definition of condensation is strictly related to the existence of single particle levels. These are not well defined in interacting systems. In order to avoid this concept we introduce the reduced density matrices and generalize the condensation criterion.

Given a N-particle system let us recall [12] that its density matrix

$$\rho(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_P, ...\mathbf{x}_N | \mathbf{x}'_1, \mathbf{x}'_2, ..., \mathbf{x}'_P, ...\mathbf{x}'_N) \tag{3.1}$$

is defined by

$$< O >= Tr\rho O \qquad Tr\rho = 1 \tag{3.2}$$

where $\mathbf{x}$ stands for the position and any other necessary quantum index, O is any observable referred to the system and <> means averaged value. In the case the system is in a pure state (for which we have the maximum information available) and is described by a vector state $|\psi>$, the density matrix ρ is

$$\rho(\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_P,...\mathbf{x}_N|\mathbf{x}'_1,\mathbf{x}'_2,...,\mathbf{x}'_P,...\mathbf{x}'_N) =$$

$$=<\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_P,...\mathbf{x}_N|\psi><\psi|\mathbf{x}'_1,\mathbf{x}'_2,...,\mathbf{x}'_P,...\mathbf{x}'_N>=$$

$$=\psi^*(\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_P,...\mathbf{x}_N)\psi(\mathbf{x}'_1,\mathbf{x}'_2,...,\mathbf{x}'_P,...\mathbf{x}'_N) \tag{3.3}$$

where$|\mathbf{x}_1,...\mathbf{x}_N>$ is a complete set for the N particle system.

Consider the case that the system cannot be represented by a vector state but has a definite temperature T owing to a thermal bath with which it weakly interacts. Its behavior can be described on the average by an ensemble of a large number of identical weakly interacting systems, m_n of which are in the state $|\psi_n>$ .If the number of copies M is made very large, the system can be considered in a mixed state in which each single state occurs with probability $P_n = m_n/M$. The density matrix ρ is then

$$\rho(\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_P,...\mathbf{x}_N|\mathbf{x}'_1,\mathbf{x}'_2,...,\mathbf{x}'_P,...\mathbf{x}'_N) =$$

$$=\sum_n P_n\psi_n^*(\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_P,...\mathbf{x}_N)\psi_n(\mathbf{x}'_1,\mathbf{x}'_2,...,\mathbf{x}'_P,...\mathbf{x}'_N) \tag{3.4}$$

The last case considered is not to be confused with the case in which the wave vector itself is a superposition of states $|\psi>=\sum_i c_i|\psi_i>$.

The reduced density matrix of order $P \leq N$ is defined as

$$h_P\left(\mathbf{x}_1,..,\mathbf{x}_P|\mathbf{x}'_1,..,\mathbf{x}'_P\right) = \frac{N!}{(N-P)!}\int d\mathbf{y}\,\rho\left(\mathbf{x}_1,..,\mathbf{x}_P,\mathbf{y}|\mathbf{x}'_1,..,\mathbf{x}'_P,\mathbf{y}\right) \tag{3.5}$$

where $\mathbf{y}$ stands for $\mathbf{x}_{P+1},..,\mathbf{x}_N$.

The diagonal part of $h_1(\mathbf{x},\mathbf{x}')$ is obviously the local density. The diagonal part of $h_2(\mathbf{x}_1,\mathbf{x}_2;\ \mathbf{x}'_1,\mathbf{x}'_2)$ is the equal time density-density correlation function.It gives the probability that, given a particle at the point $\mathbf{x}_1$, one can find another particle at point $\mathbf{x}_2$. These two functions are sufficient to describe a system with one and two body interactions.

Going back to the Bose gas, the one particle reduced density matrix h_1 is diagonal in the momentum space and its elements are the occupation numbers $n_{\mathbf{k}}$. Here the zero momentum state plays a special role and $h_1(\mathbf{x}, \mathbf{x}')$ can be accordingly written

$$h_1(\mathbf{x}, \mathbf{x}') = \frac{1}{\Omega} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')} n_{\mathbf{k}} = \frac{n_0}{\Omega} + \frac{1}{\Omega} \sum_{\mathbf{k} \neq 0} e^{-i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')} n_{\mathbf{k}} \tag{3.6}$$

$n_0 = \alpha(T)N$, $0 < \alpha \leq 1$, Ω being the volume of the system. The Riemann-Lebesgue theorem on the Fourier transforms states that

$$\lim_{x \to \pm\infty} f(x) = \lim_{x \to \pm\infty} \int_{-\infty}^{+\infty} e^{ixt} \hat{f}(t) dt = 0.$$

Therefore in the limit of an infinite system where the sum over $\mathbf{k}$ is replaced by a continuous integration in eq.(3.6)

$$\lim_{|\mathbf{x}-\mathbf{x}'| \to \infty} h_1(\mathbf{x}, \mathbf{x}') = \frac{n_0}{\Omega} = \frac{\alpha N}{\Omega} \qquad T < T_c$$

$$\lim_{|\mathbf{x}-\mathbf{x}'| \to \infty} h_1(\mathbf{x}, \mathbf{x}') = 0 \qquad T > T_c. \tag{3.7}$$

The order in momentum space given by the Bose-Einstein condensation has therefore a counterpart in configuration space. This is the appearance of a correlation in the off-diagonal matrix elements of the one particle reduced density matrix named as off-diagonal long range order (ODLRO).

This formulation is generalizable to the interacting systems, since h_1 is well defined also in the presence of interactions.

By definition a system shows condensation when the largest eigenvalue n_σ of $h_1(\mathbf{x}, \mathbf{x}')$is a finite fraction of the total number of particles. Once the eigenvalue equation

$$\int d\mathbf{x}' h_1(\mathbf{x}, \mathbf{x}') \phi_i(\mathbf{x}') = n_i \phi_i(\mathbf{x}) \tag{3.8}$$

is solved, h_1 can be written in terms of its eigenvalues and eigenfunctions

$$h_1(\mathbf{x}, \mathbf{x}') = \sum_i n_i \phi_i^*(\mathbf{x}') \phi_i(\mathbf{x}). \tag{3.9}$$

Condensation is then specified by

$$\lim_{N,\Omega \to \infty} \frac{n_\sigma}{N} = \alpha \qquad 0 < \alpha \leq 1 \tag{3.10}$$

$$\lim_{N,\Omega\to\infty} \frac{n_j}{N} = 0 \tag{3.11}$$

where $j \neq \sigma$ and $N/\Omega = const.$

It is possible to show in general [10] that the above definition of condensation, as for the Bose gas, is equivalent to appearance of long range order in the one particle reduced density matrix (ODLRO):

$$\lim_{|\mathbf{x}-\mathbf{x}'|\to\infty} h_1(\mathbf{x},\mathbf{x}') = \alpha N f^*(\mathbf{x}')f(\mathbf{x}). \tag{3.12}$$

with $\alpha N = n_\sigma$ and $f = \phi_\sigma$. We will follow a simple derivation given in ref.[13]. Condensation as defined by eqs.(3.10-3.11) leads to ODLRO when we consider the decomposition (3.9) of h_1 in terms of its eigenvalues and eigenfunctions . Viceversa in the case that eq.(3.12) is satisfied with the normalization condition

$$\int_\Omega |f(\mathbf{x})|^2 d\mathbf{x} = 1 \qquad |f(\mathbf{x})| \leq \frac{c}{\Omega^{1/2}} \tag{3.13}$$

we show that in the limit of infinite volume at constant density $f(\mathbf{x})$ tends to the eigenfunction of h_1 corresponding to the maximum eigenvalue n_σ

$$f(\mathbf{x}) \to \phi_\sigma(\mathbf{x}) \qquad \alpha N \to n_\sigma. \tag{3.14}$$

We consider the following functional of any normalized trial wave function $\phi_T = \sum_i c_i\phi_i(\mathbf{x})$, $\sum_i |c_i|^2 = 1$

$$F(\phi_T) = \int d\mathbf{x} \int d\mathbf{x}' \phi_T(\mathbf{x}') h_1(\mathbf{x},\mathbf{x}') \phi_T^*(\mathbf{x}) = \sum_i |c_i|^2 n_i \leq n_\sigma$$

where the equality holds only if $\phi_T = \phi_\sigma$.

If we choose

$$\phi_T(\mathbf{x}) = f(\mathbf{x})$$

then

$$F(f) = \alpha N + I$$

$$I = \int d\mathbf{x} \int d\mathbf{x}' f(\mathbf{x}') \left(h_1(\mathbf{x},\mathbf{x}') - \alpha N f^*(\mathbf{x}) f(\mathbf{x}')\right) f^*(\mathbf{x}) = \int d\mathbf{x} \int d\mathbf{x}' f(\mathbf{x}') \tilde{h}_1(\mathbf{x},\mathbf{x}') f^*(\mathbf{x}).$$

We next show that in the thermodynamic limit I is negligible if compared with αN. In fact

$$I \leq \int d\mathbf{x} \int d\mathbf{x}' |f(\mathbf{x}')||\tilde{h}_1(\mathbf{x},\mathbf{x}')||f^*(\mathbf{x})| \leq c^2 \int d\mathbf{r} |\tilde{h}_1(\mathbf{x},\mathbf{x}')|$$

where we have used the translational invariance: $\tilde{h}_1(\mathbf{x},\mathbf{x}') \equiv \hat{h}_1(\mathbf{r})$ is function of the relative variable only. Because of eq.(3.12) for any $\epsilon > 0$ there exists $R > 0$ such that

$$|\hat{h}_1(\mathbf{r})| < \frac{\epsilon}{2c^2} \quad if \quad |\mathbf{r}| > R$$

$$\frac{c^2 \hat{h}_M \Omega_R}{\Omega} < \frac{\epsilon}{2}$$

where $\hat{h}_M$ is the maximum of $\hat{h}_1$ in the limited domain Ω_R. Then

$$I \leq c^2 \int d\mathbf{r} |\hat{h}_1(\mathbf{r})| \leq \frac{\epsilon}{2} \int_{r>R} d\mathbf{r} + c^2 \hat{h}_M \int_{r<R} d\mathbf{r} \leq \epsilon\Omega.$$

This is clearly enough to show that

$$\lim_{\Omega,N\to\infty, N/\Omega=const} F(f) = \alpha N \leq n_\sigma \tag{3.15}$$

and there exists a macroscopic eigenvalue of h_1. Moreover any trial wave function ϕ_T satisfying the normalization condition eq.(3.13) can be obtained as a superposition of f with a function g orthogonal to it

$$\phi_T = af + bg, \qquad a^2 + b^2 = 1, \qquad \int d\mathbf{x} f^*(\mathbf{x}) g(\mathbf{x}) = 0.$$

The value (3.15) corresponds to the maximum of the functional $F(\phi_T) = a^2 \alpha N$ in this class of functions ϕ_T. The identification (3.14) follows. The argument assumes that the eigenfunction itself belongs to the specified class of wave functions.

The normalized expression of the eigenfunction corresponding to the eigenvalue n_σ obtained in the off diagonal long range limit

$$\psi(\mathbf{x}) = (\alpha N)^{1/2} \phi_\sigma(\mathbf{x}) \tag{3.16}$$

can be taken as the order parameter which goes to zero at the transition temperature, and characterizes the type of ordering occurring in superfluids, i.e. condensation in the effective single particle state, obtained as eigenfunction of the one particle reduced density matrix.

The function $\psi(\mathbf{x})$ can be considered therefore as a kind of weighted wave function for the condensate. It has a semiclassical character , i.e. its modulus squared coincides with a density rather than a probability, because of the macroscopic occupancy of such a state.

In superconductors the electrons, being fermions, cannot condense in a single particle state, because of the Pauli principle. The simplest possibility is that the two particle reduced density matrix has an eigenvalue $n_\sigma = \alpha N$ [11]. ,

Taking into account the translational invariance we can introduce the variables

$$\mathbf{r} = \mathbf{x}_1 - \mathbf{x}_2, \qquad \mathbf{r}' = \mathbf{x}_1' - \mathbf{x}_2', \tag{3.17}$$

$$\mathbf{R} = \mathbf{x}_1 - \mathbf{x}_1' + \mathbf{x}_2 - \mathbf{x}_2' \tag{3.18}$$

as h_2 depends only on three independent vectors and for simplicity we do not change the notations when we consider such dependence. On the hypothesis that there exists an eigenfunction $\phi_\sigma(\mathbf{x}_1, \mathbf{x}_2)$ of the associated eigenvalue problem

$$\int d\mathbf{x}_1' \int d\mathbf{x}_2' h_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2') = \lambda_i \phi_i(\mathbf{x}_1, \mathbf{x}_2) \tag{3.19}$$

with the corresponding macroscopic eigenvalue $n_\sigma = \alpha N$, $0 < \alpha \leq 1$, it is possible to show that the ODLRO property

$$\lim_{R\to\infty, \mathbf{r}, \mathbf{r}' < \xi} h_2(\mathbf{r}, \mathbf{r}', \mathbf{R}) = \alpha N \phi_\sigma^*(\mathbf{r}) \phi_\sigma(\mathbf{r}') \tag{3.20}$$

exists.

To show that viceversa ODLRO

$$\lim_{R\to\infty, \mathbf{r}, \mathbf{r}' < \xi} h_2(\mathbf{r}, \mathbf{r}', \mathbf{R}) = \alpha N f^*(\mathbf{r}) f(\mathbf{r}') \tag{3.21}$$

implies macroscopic occupancy of a pair state requires some care. In the case of Bose systems, in order to show that the asymptotic factorization property for the one particle reduced density matrix is equivalent to condensation, it has been enough to assume that the function f in which h_1 factorizes is normalized as the eigenfunctions of h_1 itself, i.e. the function f has to be chosen in the same class of the eigenfunctions of h_1. For the fermion case instead it is not enough that in the limit of infinite volume $f(\mathbf{r})$ is normalized in the same way as the eigenfunctions of h_2. When the function f in which the two particle reduced density matrix asymptotically factorizes is chosen in the class of functions f such that $f(\mathbf{x}_1 - \mathbf{x}_2) = 0$ if $|\mathbf{x}_1 - \mathbf{x}_2| > \xi$, the argument essentially goes through as for h_1 [13]. Physically this means that f varies in the restricted class of functions which describe two-particle bound states. We can include in this class exponentially decreasing functions. If this is not the case for large separation between $\mathbf{x}_1$ and $\mathbf{x}_2$,$\phi_\sigma(\mathbf{x}_1, \mathbf{x}_2)$ factorizes in the product of two single particle states. $h_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2')$ is then approximated by products of h_1's at different points as for a Fermi gas. Eigenvalues of the order of N for h_2 cannot be obtained in this case, because the eigenvalues of h_1 are all finite. The distance ξ between $\mathbf{x}_1$ and $\mathbf{x}_2$ beyond which $\phi_\sigma \sim 0$, corresponds to the coherence length.

In the previous section we have seen that a phenomenological explanation of the superconductivity implies condensation. We have now achieved the result that fermions may condense provided pair formation occurs [11]. Therefore any microscopic theory of superconductivity showing condensation must be based on electron pair formation as indeed the B.C.S. theory [14] does. The order parameter is again related to the eigenfunction of h_2 corresponding to the macroscopic eigenvalue and can be considered as a weighted pair wave function:

$$\chi(\mathbf{x}_1, \mathbf{x}_2) = (\alpha N)^{1/2} \phi_\sigma(\mathbf{x}_1, \mathbf{x}_2). \tag{3.22}$$

As we shall see in the microscopic theory the gap energy is strictly related to χ. Indeed Gor'kov[15] assumed that the actual order parameter is the integrated quantity

$$\Delta(\mathbf{x}_1) = \int V(\mathbf{x}_1, \mathbf{x}_2) \chi(\mathbf{x}_1, \mathbf{x}_2) d(\mathbf{x}_1 - \mathbf{x}_2) = -g\chi(\mathbf{x}_1, \mathbf{x}_1) \tag{3.23}$$

where $V(\mathbf{r})$ is the attractive potential leading to superconductivity, assumed to be strongly peaked at $\mathbf{r} = 0$, and

$$g = -\int d\mathbf{x} V(\mathbf{x})$$

defines the coupling constant. In phenomenological theories [16] instead the order parameter ψ is normalised in such a way as to make $|\psi|^2$ equal to the superconducting electron density n_s i.e.

$$\psi(\mathbf{x}) = Z^{1/2}\Delta(\mathbf{x}) \tag{3.24}$$

where Z is the normalizing constant such that $|\psi|^2 = n_s$ and $\mathbf{x}$ represents the center of mass of the bound pair. These positions are altogether consistent with the phenomenology introduced in chapter 2.

4 ORDER PARAMETER AND SYMMETRY

The discussion of the criterion for condensation has enabled us to introduce the important concept of the order parameter, which is maximum at zero temperature, goes to zero at the critical point and is zero above it, this being a common feature of all second order phase transitions [8, 17].

These transitions are characterised by a discontinuous change of the symmetry properties of the system at the critical temperature. The phase at high temperature is more symmetric than the phase at low temperature. For example an isotropic ferromagnet is invariant under space rotations transformations above its Curie point. Below T_c, where the spontaneous magnetization (order parameter in this case) is different from zero, the system is not invariant under generic rotations because of the privileged direction of the spontaneous magnetization itself i.e. the ordered phase is less symmetric. However small the spontaneous magnetization is, as long as it is different from zero, the larger symmetry is not restored.

The symmetry of a system is represented by the group of transformations which leave invariant the Hamiltonian. These symmetry transformations are expressed in a given representation as operators that act on the Hilbert space of the system and have the property of commuting with the Hamiltonian.

The eigenstates of a given representation transform into each other under the action of the symmetry group. The symmetric phase has a ground state which is not degenerate and hence is invariant under the transformations. Under given circumstances the ground state is degenerate and the selection of one among all possible degenerate states (choice of the direction of the spontaneous magnetization in ferromagnets) gives raise to a phase which has a lower symmetry than the original Hamiltonian. This phenomenon is known as the spontaneous symmetry breaking [18] in the sense that the invariance properties of the system still survive but a particular solution is not invariant. The symmetry of the ordered phase remains different up to the transition point i.e. as long as the order parameter is different from zero. As the critical point must have the symmetry of both phases, the symmetry group of the disordered phase (more symmetric) must contain the symmetry group of the ordered phase (less symmetric phase).

Let us now turn our attention to the invariance properties broken in the superconductive phase.

In quantum mechanics the conservation of charge is related to the invariance under the global phase transformation $e^{i\theta\hat{N}}$, $\hat{N}$ being the total number operator, which commutes with the hamiltonian. The wave function of the an N-particle system transforms as

$$\psi_N \rightarrow e^{iN\theta}\psi_N \tag{4.1}$$

where θ is between 0 and 2π. According to their definition the density matrix and all the reduced density matrices are invariant under the global phase transformations. This is enough to characterize the physical properties of a normal system. In the previous section we have seen that in the case of superconductors instead the existence of a condensation of electron pairs in a single state is the condition to be imposed in order to explain the phenomenology. This condensation phenomenon is characterised by the appearance of off-diagonal long range order in the two particle reduced density matrix and by the possibility of factorizing it in terms of the pair wave function ψ which we take as order parameter. Hence, while the two particle reduced density matrix h_2 remains invariant under global phase transformations, the order parameter transforms as

$$\psi \rightarrow e^{i2\theta}\psi.$$

Now a well sound assumption is that the superconducting state is well approximated by a coherent macroscopic occupation of the pair state at fixed phase rather than at fixed N, giving rise to a spontaneous symmetry breaking.

For the superfluid Helium (^4He) the above argument can be repeated using the one particle reduced density matrix h_1.

Until now we have considered only global phase transformation, i.e. the phase θ is independent of space and time. As it is well known from the electrodynamics local gauge invariance leads us to introduce the scalar and the vector potential V and $\mathbf{A}$ and their transformations with a space and time dependent scalar function ϕ

$$\mathbf{A} \rightarrow \mathbf{A} + \nabla\phi(x,t) \tag{4.2}$$

$$V \rightarrow V - \frac{1}{c}\frac{\partial\phi(x,t)}{\partial t}. \tag{4.3}$$

Since the order parameter ψ obtained from the factorization of the two particle reduced density matrix h_2 , corresponds to a weighted "single particle wave function" describing the distribution of the center of the mass of the bound pair , under local gauge transformation it transforms according to

$$\psi \rightarrow e^{i(e^*/\hbar c)\phi(x,t)}\psi \tag{4.4}$$

e^* being the effective electric charge of the charge carriers ($e^* = 2e$ for the present case).

Now we want to show that our interpretation of the order parameter as a semi-classical wave function is sufficient to explain all the "super" effects.

We start from the expression of the Schrödinger equation for a particle in the presence of a scalar and vector potential:

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{1}{2m}\left(\frac{\hbar}{i}\nabla - \frac{e^*}{c}\mathbf{A}\right)^2\psi + e^*V\psi \tag{4.5}$$

The general solution to this equation can be written as

$$\psi = \psi_0 exp\left(-i\frac{e^*}{\hbar}\int_{t_0}^{t} V dt' + \frac{ie^*}{c\hbar}\int_{x_0}^{x} \mathbf{A}\cdot d\mathbf{l}\right) \tag{4.6}$$

ψ_0 being the wave function in the absence of external fields. The phase θ_0 of the wave function is changed into

$$\theta = \theta_0 - \frac{e^*}{\hbar}\int_{t_0}^{t} V dt' + \frac{e^*}{c\hbar}\int_{x_0}^{x} \mathbf{A}\cdot d\mathbf{l}. \tag{4.7}$$

Using the general expression for the current in quantum mechanics we get the supercurrent

$$\mathbf{J}_s = e^*|\psi_0|^2\frac{\hbar}{m}\left(\nabla\theta - \frac{e^*}{c\hbar}\mathbf{A}\right) = e^*|\psi_0|^2\frac{\hbar}{m}\left(\nabla\theta_0 - \frac{e*}{\hbar}\int \nabla V dt'\right) \tag{4.8}$$

Whenever **A** is equal to zero, the superfluid current is given by

$$\mathbf{J}_s = \frac{e^*|\psi_0|^2\hbar}{m}\nabla\theta. \tag{4.9}$$

In the presence of a vector potential we choose the gauge $div\mathbf{A} = 0$ which, when the system is isolated, gives

$$div\mathbf{J}_s = 0 = \frac{\hbar}{m}\nabla^2\theta \tag{4.10}$$

that is equivalent to $\theta = const$. The London relation eq.(2.10) between the current and the vector potential then follows from eq.(4.8), provided $|\psi_0|^2 = n_s$ as hypothesized for the normalization of the order parameter in the previous chapter.

The quantization of the flux [19, 20] and the Josephson effect[21, 22, 23] are also easily derived from the expression for the current .

Let us consider a superconducting ring below its transition temperature. We consider a closed contour C well inside the ring. Along the contour the current must be zero because the field cannot penetrate in the bulk. Hence performing the contour integration we obtain

$$\int_C \mathbf{J}_s\cdot d\mathbf{l} = \int_C e^*|\psi_0|^2\frac{\hbar}{m}\left(\nabla\theta - \frac{e^*}{c\hbar}\mathbf{A}\right)\cdot d\mathbf{l} = e^*|\psi_0|^2\frac{\hbar}{m}\left(\Delta\theta - \frac{e^*}{c\hbar}\Phi(B)\right) = 0 \tag{4.11}$$

where $\phi(B)$ is the magnetic flux trapped inside the ring. Since the wave function must be single valued $\Delta\theta = 2\pi n$ and the flux is quantized:

$$\Phi(B) = n\frac{ch}{e^*} \tag{4.12}$$

n being an integer.

The experiments give $e^* = 2e$ [19] according to the basic assumption of the pair condensation .

We now briefly discuss the Josephson effect. It may be useful to make again an analogy with the ferromagnets. In a ferromagnet below its Curie point the order parameter is the spontaneous magnetization M_1 which breaks the invariance under rotations, setting a preferred orientation in space. Another ferromagnet with a magnetization M_2 oriented at an angle θ with respect to the previous one, when sufficiently near, gives rise to an interaction energy $U(\theta) = M_1 M_2 cos(\theta)$. In the case of two superconductors we may apply the same concept. The complex order parameter may also be viewed as a two component vector. In the phase of broken symmetry , a choice for ψ corresponds to a preferred orientation in the complex plane. Then it is natural to write the interaction energy of two superconductors , separated by a insulating junction , as a periodic function of the phase difference $\theta_1 - \theta_2$ of the order parameter, exactly as for the ferromagnets. In order to convince ourselves of the presence of such an energy term in the Josephson junction we add the following considerations. If we let the thickness d of the film of the insulating layer become very large ($d \gg \xi$) the system is made of two independent isolated superconductors, each one with a constant phase uncorrelated to the other one , as can be derived from the condition $\nabla^2\theta = 0$ previously discussed. On the other hand when the thickness d goes to zero, the two superconductors will tend to behave as a single one with an overall constant phase and the phase difference between the two must go to zero. There is therefore an interaction energy $U(\theta_1 - \theta_2)$ which goes to zero as $d \gg \xi$ and becomes important when $d \ll \xi$. U must be an even periodic function of θ, $U = C\ cos\theta$. When the two superconductors are separated by a small distance d (usually d is of the order $10-50\AA$ much less than the penetration lenght λ and the coherence distance ξ over which the pair wave function extends) we may approximate the phase difference as $\theta_1 - \theta_2 = d|\nabla\theta|$. From the gauge invariance we know that only the combination of the phase gradient and the vector potential is physically meaningful. Hence ,using the general fact that the derivative with respect to the vector potential gives the current , we may write

$$\mathbf{J}_s = \frac{dU(\theta)}{d\nabla\theta} = \mathbf{J}_c sin(\theta) \tag{4.13}$$

from which we see that a supercurrent flows across the junction i.e. pairs can tunnel from one side to the other of the junction without a d.c. voltage. The maximum Josephson current $\mathbf{J}_c$ can be determined by microscopic calculations only.

The presence of an electromagnetic field modifies the phase of the pair wave function according to eq.(4.7). A scalar potential V gives rise to an a.c. Josephson current with frequency

$$\dot{\theta} = -\frac{e^* V}{\hbar}. \tag{4.14}$$

This current oscillates very rapidly due to appearance of the Planck constant and therefore averages to zero. Combining two Josephson junctions in a circuit it is possible to study interference effects on the outcoming current as a function of the magnetic flux through the loop in units of the quantum hc/e^*.

The experimental observation of quantization of flux [19], of the d.c. Josephson current and the interference effects in the Josephson junctions [23] is the most direct evidence of the appearance of quantum phenomena on macroscopic level via the coherent macroscopic occupation of a single pair state due to the off diagonal long range order.

5 LANDAU THEORY OF SECOND ORDER PHASE TRANSITIONS. ITS LIMIT OF VALIDITY

In the previous sections we have seen that the transition from normal to superconducting state is of the second order at zero external magnetic field. Below the critical temperature the superconducting phase is characterized by a non zero value of the order parameter ψ, which has the meaning of the wave function describing the electron pairs in the condensate.

On the assumption that the thermodynamic potential is analytical with respect to the order parameter near the transition point, it is possible to build up the phenomenological theory of the second order phase transitions due to Landau [8, 17], which is the general form of all the mean field approximation treatments.

When we discussed the Josephson effect, we made the analogy between a superconductor and a ferromagnet below its Curie point. In both cases the spontaneous symmetry breaking occurs in the sense that the phase of ψ or the direction of the spontaneous magnetization is fixed among all degenerate configurations.

In the case of magnetic transitions an infinitesimal external magnetic field is necessary in order to fix the direction of the magnetization.

In the language of thermodynamics the magnetic field and the magnetization are conjugate variables. All physical properties of a ferromagnet can be described once we have introduced the free energy as a functional of the temperature T and the magnetic field $h(\mathbf{x})$. The magnetization per unit volume $m(\mathbf{x})$, i.e. the order parameter is defined as the functional derivative of the free energy with respect to the magnetic field h

$$m(\mathbf{x}) = -\frac{\delta F(T,h)}{\delta h(\mathbf{x})}. \tag{5.1}$$

The spontaneous magnetization, i.e. the order parameter is obtained in the limit of zero external field. We consider the thermodynamic potential as a function of the order parameter by performing a Legendre transformation

$$\tilde{F}(T,m) = F(T,h(m)) + \int d\mathbf{x} m(\mathbf{x})h(\mathbf{x}) \tag{5.2}$$

from which the other conjugation relation follows

$$\frac{\delta \tilde{F}(T,m)}{\delta m(\mathbf{x})} = h(\mathbf{x}). \tag{5.3}$$

From now on we will consider the thermodynamic potential $\tilde{F}(T,m)$ and set $F(T,m) \equiv \tilde{F}(T,m)$.

Going back to superconductivity it is possible to associate to the order parameter an external conjugate field, even though its physical interpretation is no more as direct as in the magnetic phenomena. Accordingly we introduce the free energy for a superconducting sample as a functional of the temperature T and of a complex external field η and define the order parameter ψ as the functional derivative of the free energy with respect to this field η in the same way as done in eq.(5.1). It is again convenient to perform a Legendre transformation by the introduction of the term

$$\int d\mathbf{x}\,(\eta(\mathbf{x})\psi^*(\mathbf{x}) + \eta^*(\mathbf{x})\psi(\mathbf{x}))$$

and consider the thermodynamic potential as functional of the order parameter ψ instead of the external field η.

The main assumption of the Landau theory, which for superconductors goes under the name of Landau-Ginzburg [16], is that the thermodynamic potential per unit volume near the transition point can be expanded in a powers series of the order parameter and of the gradient of the order parameter

$$F_s(T,\psi) = F_n + \frac{1}{V}\int d\mathbf{x}\left(a|\psi|^2 + \frac{b}{2}|\psi|^4 + c|\nabla\psi|^2 + ...\right). \tag{5.4}$$

where the subscripts s and n stand for superconductive phase and normal phase respectively. $|\psi|^2$ and $|\nabla\psi|^2$ can only appear in the expansion, since F cannot depend on the phase of the order parameter. The coefficient a,b and c must be regular and smooth functions of T. Since in the expansion we retain a term proportional to the gradient square only, we allow for small space variations of ψ or small k components. This term comes from the variations of the order parameter and the current flow. It must enter the expansion with a positive sign because at equilibrium the system tends to be homogenous: c is therefore assumed to be a positive constant.

In order to preserve local gauge invariance the kinetic term in the expansion for the free energy in the presence of an external magnetic field becomes

$$|\left(\nabla - i\frac{e^*}{\hbar c}\mathbf{A}\right)\psi|^2. \tag{5.5}$$

Further to have the complete expression for the thermodynamic potential in the presence of a magnetic field we add a term due to the energy density of the field $\frac{\mathbf{H}^2}{8\pi}$. To avoid confusion with the coefficient c introduced in eq.(5.4), from now on we put the light velocity equal to unity.

By varying the thermodynamic potential with respect to ψ^* and $\mathbf{A}$ with the gauge choice $div\mathbf{A} = 0$ one obtains the equations for the order parameter and the current

$$a\psi + b|\psi|^2\psi - c|\nabla - i\frac{e^*}{\hbar}\mathbf{A}|^2\psi = \eta \tag{5.6}$$

$$\mathbf{J} = i\frac{e^*c}{\hbar}\left(\psi\left(\nabla + i\frac{e^*}{\hbar}\mathbf{A}\right)\psi^* - c.c\right) = -\frac{1}{4\pi}\nabla^2\mathbf{A}. \tag{5.7}$$

Variation of the free energy with respect to ψ leads to the complex conjugate of eq.(5.6). Eq.(5.7) is the usual expression relating the vector potential and the current density. We note in addition that Eq.(5.7) is equivalent to eq.(4.8) for the supercurrent provided we identify the parameter $c = \hbar^2/2m$.

In the absence of an external electromagnetic field eq.(5.6) reduces to

$$(a + b|\bar{\psi}|^2)\bar{\psi} = \eta. \tag{5.8}$$

In the limit $\eta \to 0$, $\bar{\psi} \to \psi_0$ and the order parameter has two homogenous solutions

$$\psi_0 \equiv 0, \qquad |\psi_0|^2 = -\frac{a}{b}. \tag{5.9}$$

We want that the first trivial solution applies above T_c and therefore $a > 0$ for $T > T_c$, since a small variation of ψ with respect to the zero value must cost a positive energy and increase F. The second solution instead applies below T_c. We need therefore $a < 0$ for $T < T_c$. The Landau choice is $a = a'(T - T_c)$ with constant $a' > 0$. At T_c b must be positive and therefore Landau assumed it constant around T_c. The homogenous order parameter ψ_0 now reads

$$|\psi_0|^2 = -\frac{a'}{b}(T - T_c). \tag{5.10}$$

Substituting this solution in eq.(5.4) we obtain the difference between the thermodynamic potential for the normal and the superconductive system:

$$F_n - F_s = \frac{a'^2}{2b}(T - T_c)^2 = \frac{H_c^2(T)}{8\pi}. \tag{5.11}$$

The last equality has been obtained by means of eq.(2.5). The temperature dependence of the critical field near the critical temperature given by eq.(2.1) shows that the superconductive transition is well represented as a second order phase transition in the Landau approximation. The specific heat jump we discussed in section II, now reads

$$\Delta C = \frac{a'^2 T_c}{b} = \frac{T_c}{4\pi}\left(\frac{\partial H_c(T)}{\partial T}\right)^2_{T=T_c} . \tag{5.12}$$

The Ginzburg-Landau parameters a', b are then related to physical quantities as the critical field and the specific heat jump and can be fitted by experiments.

Up to now we considered homogenous solutions only. If we allow for small space variation of the order parameter either due to fluctuations or to the presence of an external field, two lengths characterize the Landau-Ginzburg theory, the penetration depth λ and the coherence distance ξ.

As already stressed in chapter 4 the London relation (eq.(2.10)) between the current and the vector potential is obtained with the penetration depth λ given by

$$\lambda^2 = \frac{mc^2}{4\pi e^{*2}}\frac{1}{|\psi_0|^2} = \frac{mc^2}{4\pi e^{*2}}\frac{b}{a'|T-T_c|}$$

provided $|\psi|^2$ can be approximated by $|\psi_0|^2$ in the range of variation of $\mathbf{A}$. Otherwise the electromagnetic penetration is no longer exponential and the rise of ψ to the value ψ_0 is no more abrupt as required by the Landau theory.

We discuss now the non homogenous case allowing for the fluctuations of the order parameter. Using again the analogy with ferromagnets, we write the complex order parameter in terms of its real and imaginary parts, which behave as the components of a two dimensional vector in the complex plane $\psi = \psi_1 + i\psi_2$. From eq.(5.6) and its complex conjugate it is easy to derive the equations for ψ_1 and ψ_2 at $\mathbf{A} = 0$

$$a\psi_1 + b(\psi_1^2 + \psi_2^2)\psi_1 - c\nabla^2\psi_1 = \eta_1 \tag{5.13}$$

$$a\psi_2 + b(\psi_1^2 + \psi_2^2)\psi_2 - c\nabla^2\psi_2 = \eta_2 \tag{5.14}$$

having set $\eta_1 = (\eta + \eta^*)/2$ and $\eta_2 = (\eta - \eta^*)/2i$. Eq.(5.9) determines the homogenous value of the order parameter below T_c but a phase factor. We now choose a solution by taking $\eta_2 \equiv 0$, $\eta_1 \to 0$, fixing the gauge with real homogenous solution of eqs.(5.13-5.14): $\psi_1 = \psi_0$ and $\psi_2 = 0$. On the assumption of small fluctuations of the order parameter with respect to the equilibrium value, we set $\psi_1 = \bar{\psi} + \delta\psi_1$, $\psi_2 = \delta\psi_2$ and the linearized form of eqs.(5.13-5.14) reads

$$(a + 3b\bar{\psi}^2)\delta\psi_1 - c\nabla^2\delta\psi_1 = \delta\eta_1 \tag{5.15}$$

$$(a + b\bar{\psi}^2)\delta\psi_2 - c\nabla^2\delta\psi_2 = \delta\eta_2. \tag{5.16}$$

The equations (5.8) and (5.9) imply that the homogenous fluctuations of the imaginary part of ψ do not cost energy $a + b\bar{\psi}^2 = (\eta_1/\bar{\psi}) \to 0$ when $\eta_1 \to 0$, i.e. they are massless whenever the homogenous solution $|\psi_0|^2 = -a/b$ is stable. This is clearly understood by considering that within our gauge choice the fluctuations of ψ_2 correspond to the fluctuations of the phase of the order parameter, which cannot cost energy due to the gauge invariance of the theory. In fact by writing $\psi = |\psi|e^{i\theta} \sim (|\psi_0| + \delta|\psi|)(1 + i\theta) \sim |\psi_0| + \delta|\psi| + i|\psi_0|\theta$, we see that eq.(5.16) for ψ_2 when $\delta\eta_2 = 0$ is equivalent to the eq.(4.10) for the phase of the order parameter.

According to the general theory of linear response we introduce the correlation function $f_{\psi,\parallel}$ and $f_{\psi,\perp}$ associated with the "longitudinal" and "transverse" fluctuations of ψ as functional derivatives of ψ_1 and ψ_2 with respect to η_1 and η_2

$$f_{\psi,\parallel}(\mathbf{x}, \mathbf{x}') = k_B T \frac{\delta\psi_1(\mathbf{x})}{\delta\eta_1(\mathbf{x}')}. \tag{5.17}$$

$$f_{\psi,\perp}(\mathbf{x}, \mathbf{x}') = k_B T \frac{\delta\psi_2(\mathbf{x})}{\delta\eta_2(\mathbf{x}')}. \tag{5.18}$$

Considering the mathematical property

$$\frac{\delta\eta_{1,2}(\mathbf{x})}{\delta\eta_{1,2}(\mathbf{x}')} = \delta(\mathbf{x} - \mathbf{x}') \tag{5.19}$$

from eqs.(5.15) and (5.16) we obtain the equations for the correlation functions $f_{\psi,\parallel}$ and $f_{\psi,\perp}$

$$(-2a - c\nabla^2) f_{\psi,\parallel} = k_B T \delta(\mathbf{x} - \mathbf{x}') \tag{5.20}$$

$$((\eta_1/\bar{\psi}) - c\nabla^2) f_{\psi,\perp} = k_B T \delta(\mathbf{x} - \mathbf{x}') \tag{5.21}$$

with $\bar{\psi}(\eta_1) \to \psi_0$ when $\eta_1 \to 0$. Because of translational invariance we can solve these equations by standard methods using the Fourier transforms. In fact, if we define

$$f_{\psi,\parallel}(\mathbf{k}) = \int d(\mathbf{x}-\mathbf{x}')f_{\psi,\parallel}(\mathbf{x},\mathbf{x}')\, e^{-i\mathbf{k}(\mathbf{x}-\mathbf{x}')} \tag{5.22}$$

$$f_{\psi,\perp}(\mathbf{k}) = \int d(\mathbf{x}-\mathbf{x}')f_{\psi,\perp}(\mathbf{x},\mathbf{x}')\, e^{-i\mathbf{k}(\mathbf{x}-\mathbf{x}')} \tag{5.23}$$

we get from eqs.(5.20) and (5.21)

$$f_{\psi,\parallel}(\mathbf{k}) = k_B T \frac{1}{-2a+ck^2} = (k_B T/c)\frac{1}{\xi^{-2}+k^2} \tag{5.24}$$

$$f_{\psi,\perp}(\mathbf{k}) = k_B T \frac{1}{(\eta_1/\bar{\psi})+ck^2} \tag{5.25}$$

where we have introduced the temperature dependent length for the fluctuations of the amplitude of the order parameter

$$\xi^{-2} = \frac{-2a}{c} = \frac{2a'}{c}|T-T_c| \equiv \xi_0^{-2}\frac{|T-T_c|}{T_c} \qquad T<T_c$$

$$\xi^{-2} = \frac{a}{c} = \frac{a'}{c}|T-T_c| \qquad T>T_c \tag{5.26}$$

$\xi_0 = (c/2a'T_c)^{1/2}$ being the zero temperature coherence distance. The value of $\xi(T)$ gives the characteristic distance over which varies the order parameter. The ratio K of the two characteristic lengths λ and ξ is the Landau-Ginzburg parameter which characterizes the classification of superconductors in first and second kind as we discussed in section II. This quantity can be directly connected to experimentally observable quantities

$$K = \frac{\lambda(T)}{\xi(T)} = \frac{2^{1/2}e^*}{\hbar}\lambda^2(T)H_c(T) \tag{5.27}$$

as it can be easily derived by using eq.(5.11) and eq.(5.26) and the expression for λ.

Eq.(5.25) allows us to discuss the role of the phase fluctuations. An estimate of the magnitude of the transverse phase fluctuations is given by summing over all wave vectors q the correlation function $f_{\psi,\perp}(q)$

$$<|\delta\psi_\perp|^2> = \sum_q f_{\psi,\perp}(q) = S_d\int_0^\Lambda dq \frac{q^{d-1}}{(\eta_1/\bar{\psi})+cq^2} =$$

$$= (S_d/c)\frac{1}{d-2}\left(\Lambda^{(d-2)/2} - (\eta_1/c\bar{\psi})^{(d-2)/2}\right), \quad \eta_1 \to 0. \qquad (5.28)$$

Λ being an ultraviolet cut-off of the order of the Fermi wave vector and S_d is the solid angle in d dimensions. We see that in $d < 2$ when $\eta_1 \to 0$ the transverse fluctuations become infinitely large unless $\psi_0 \equiv 0$, i.e. the order parameter is identically vanishing. This result is the content of the theorem first stated by Mermin and Wagner [24] according to which spontaneous symmetry breaking cannot exist in systems with number of components of the order parameter $n \geq 2$ and dimension $d \leq 2$.

We now briefly discuss the general validity of the theory of second order phase transitions so far analysed. From the expression of the correlation length eq.(5.26) we see that when approaching the critical point the distances over which the order parameter fluctuates become infinitely large, while the order parameter itself goes to zero, the assumption of neglecting fluctuations or considering them small is no more valid. The Landau theory is valid in a region not too close the critical point. In order to determine the size of such a region we can use the Ginzburg criterion. At temperature T the modulus square of the averaged fluctuation of the order parameter can be estimated in terms of its Fourier components with wave vector $q < \xi^{-1}(T)$

$$< |\delta\psi|^2 > = \sum_{q<\xi^{-1}(T)} < |\delta\psi_q|^2 > = \sum_{q<\xi^{-1}(T)} f_{\psi,||}(q). \qquad (5.29)$$

The Ginzburg criterion simply states that the Landau theory is valid as long as

$$\frac{< |\delta\psi|^2 >}{\psi_0^2} = \frac{T_c}{2(\Delta C/k_B)\xi_0^2(2\pi)^d(T_c - T)} \int_0^{\xi^{-1}(T)} d^dq \frac{1}{q^2 + \xi^{-2}(T)} < 1 \qquad (5.30)$$

which means that the contribution of fluctuations is small with respect to the homogenous solution ψ_0. The evaluation of the ratio eq.(5.30) gives in d=3

$$\frac{|T - T_c|}{T_c} \gg \frac{|T_0 - T_c|}{T_c} \sim \frac{1}{(\Delta C/k_B)^2} \frac{1}{\xi_0^6} \qquad (5.31)$$

from which we see that the Landau-Ginzburg theory is valid for temperatures which differ from the critical point more than a certain value $|T_0 - T_c|$ which depends on the parameters of the system. In particular we stress the sixth power dependence on the zero temperature coherence distance ξ_0.

In ordinary superconductors ξ_0 is quite large of the order of $10^4 \AA$ and $\Delta C \sim 10^4 erg/cm^3 degr$. With these values $|T_0 - T_c| \sim 10^{-15} T_c$. It is outside experimental possibilities to observe any deviations from the Landau-Ginzburg theory.

In two dimensions however the effect of fluctuations is enhanced. This is apparent from the eq.(5.29) for the magnitude of the fluctuations of the order parameter. Effective two dimensional systems are films whose thickness d is less than the coherence distance ξ $(d < \xi)$. In this case the inverse sixth power dependence from the zero temperature coherence distance is changed into

$$\frac{|T_0 - T_c|}{T_c} \sim \frac{1}{(\Delta C/k_B)\xi_0^2 d}. \tag{5.32}$$

To going from three dimensions to two dimensions we made the the substitution

$$\frac{1}{V}\sum_q = \frac{1}{(2\pi)^3}\int d^3q \rightarrow \frac{1}{d}\frac{1}{(2\pi)^2}\int d^2q$$

where d takes care of the reduced effective dimension of the region of integration in eq. (5.29). A further increase of the effect of the fluctuations is due to the presence of impurities in the superconductive sample. In systems where there is a strong concentration of impurities (dirty superconductors) ξ_0 is usually much smaller ($\xi_0 \sim 10^2$Å) than in pure samples (clean superconductors) ($\xi_0 \sim 10^4$Å). To qualitatively understand the origin of the change of the value of the zero temperature coherence distance we observe that in clean systems the electronic motion is ballistic whereas in dirty samples the electrons diffuse to a distance $R(t)$ in a time t according to the diffusion law $< R^2(t) >= Dt$, where $D = v_F l/3$ is the diffusion coefficient and l the mean free path. The energy involved in the correlation of the electrons leading to superconductivity is of the order of $k_B T_c$ which is also proportional to the gap Δ_0 of the excitations spectrum. In clean systems the electrons at the Fermi surface are correlated and hence can form a pair over a typical distance $\xi_{0,c} \sim \hbar v_F / k_B T_c$. In dirty superconductors electrons at the Fermi surface are correlated over times of the order of $\tau \sim \hbar/k_B T_c$ and the zero temperature coherence distance is estimated by the distance over which a wave packet may diffuse $\xi_{0,d} \sim (D\hbar/k_B T_c)^{1/2} = (\hbar v_F l/3k_B T_c)^{1/2} \sim (\xi_{0,c} l)^{1/2}$. The subscripts c and d stand for clean and dirty respectively. The mean free path is typically of the order of $10^2 \AA$.

Various effects due to fluctuations have been considered [25], in particular Glover [26] used thin films of amorphous bismuth in order to take the best advantage of the two previous effects. He found that when approaching T_c from the high temperature side as a sign of superconductive fluctuations and as a precursor effect of superconductivity itself, the conductivity σ diverges with a characteristic temperature behaviour. We shall discuss this effect in the next section.

In the new high T_c superconductors the value of the zero temperature coherence distance [27] as measured by critical field and fluctuation conductivity is of the order of $10\AA$ making plausible the possibility to observe deviations from mean field behaviour and fluctuation effects also in three dimensional clean samples.

6 PARACONDUCTIVITY

So far we have limited our discussion to the equilibrium properties of a superconductor near the critical point and we did not consider the time dependence of the order parameter. However when we want to study the transport properties it is necessary to know how the fluctuating order parameter relaxes towards its equilibrium value. According to the general principles of the thermodynamics of non equilibrium processes [8], the rate of variation of the order parameter for small deviations out of equilibrium is proportional to the conjugate field, i.e.

$$\frac{\partial \psi}{\partial t} = -\frac{1}{\gamma}\frac{\delta F(\psi)}{\delta \psi^*} \tag{6.1}$$

where the quantity $1/\gamma$ is the kinetic coefficient.

The equation for the order parameter we have written in the case of non homogenous fluctuations now reads

$$a\psi + b|\psi|^2\psi - c\nabla^2\psi = -\gamma\frac{\partial \psi}{\partial t} \tag{6.2}$$

which in the presence of an electromagnetic field changes accordingly to the gauge invariant form

$$\nabla^2 \to \left(\nabla - i\frac{e^*}{\hbar}\mathbf{A}\right)^2, \quad \frac{\partial}{\partial t} \to \frac{\partial}{\partial t} + i\frac{e^*}{\hbar}V$$

If the order parameter is conserved as for example in the ferromagnetic transition, γ^{-1} is replaced by $\lambda\nabla^2$, which implies that $\lim \psi_k = 0$ when $k \to 0$.

The presence of fluctuations of the order parameter near and above the critical temperature manifests in an excess conductivity due to the direct acceleration of the fluctuating superconducting pairs in the presence of a electric field. This phenomenon is called paraconductivity and was experimentally observed by Glover [26]. The experiment carried out by Glover was explained by the microscopic theory developed by Aslamazov and Larkin within the Green function approach [28]. We now see that this result can be more heuristically derived in terms on the eq.(6.2) for the time dependent fluctuations of the order parameter [29, 30, 31].

Assuming that fluctuations are small eq.(6.2) can be linearized. Above T_c we write the fluctuating order parameter as $\psi = |\psi|e^{i\theta}$ and substitute it in eq.(6.2). The real and imaginary parts of this equation in the presence of an electric field result in the two uncoupled equations when the magnetic field is absent

$$(a - c\nabla^2)|\psi| = -\gamma\frac{\partial}{\partial t}|\psi| \tag{6.3}$$

and

$$\gamma\left(\dot{\theta} + \frac{e^*}{\hbar}V\right) = c\nabla^2\theta. \tag{6.4}$$

Below T_c the linearization procedure around the equilibrium value ψ_0 replaces a with $-2a$ in eq.(6.3). When the Josephson eq.(4.14) is satisfied, eq.(6.4) gives $\nabla^2\theta = 0$ and all the results of chapter IV are recovered together with

$$\dot{\mathbf{v}}_s = \frac{\hbar}{m}\nabla\dot{\theta} = \frac{e^*}{m}\mathbf{E}. \tag{6.5}$$

Eq.(6.3) gives the relaxation towards the equilibrium of the Fourier component $\mathbf{k}$ of the order parameter $\psi(\mathbf{k}, t)$

$$\psi(\mathbf{k}, t) = \psi(\mathbf{k})e^{-t/\tau_{\mathbf{k}}} \tag{6.6}$$

with a relaxation time $\tau_{\mathbf{k}}$ given by

$$\tau_{\mathbf{k}} = \frac{\gamma}{c}\frac{1}{\xi^{-2}(T)+k^2} = \frac{1}{\tau_{LG}^{-1}+(c/\gamma)k^2} \tag{6.7}$$

where we have introduced the Ginzburg-Landau relaxation time τ_{LG}:

$$\tau_{LG}^{-1} = \frac{c\xi^{-2}}{\gamma} = \frac{\gamma^{-1}}{\chi} = \frac{a'}{\gamma}(T-T_c). \tag{6.8}$$

The relaxation rate of the order parameter is determined by the ratio of the kinetic coefficient to the "susceptibility" χ ($\chi = 1/a$, $T > T_c$; $\chi = -1/2a$, $T < T_c$) and goes to zero at the critical point. According to the conventional theory of the critical slowing down the kinetic coefficient of the order parameter γ^{-1} is assumed to remain finite at the critical point i.e. it is taken constant in the nearby region. The scaling theory of the critical phenomena shows that when T is sufficiently near T_c in addition to a change of the power law behaviour as a function of $T-T_c$ the kinetic coefficient also become critical. We will not discuss this point in these lectures.

In order to obtain the conductivity due to fluctuations, from the expression of the related current

$$\mathbf{J} = e^*|\psi|^2\frac{\hbar}{m}\nabla\theta,$$

we can use the equation (6.6) for the order parameter and eq.(6.5) for the phase θ. For each mode k the average of $|\psi(k)|^2$ (as given by the correlation function $f_\psi(k)$ calculated in the previous section) lasts as a super-density over the characteristic time yielded by the time averaging

$$\frac{\tau_k}{2} = \frac{\int_0^\infty dt\; te^{-2t/\tau_k}}{\int_0^\infty dte^{-2t/\tau_k}}.$$

We then get for the conductivity due to the fluctuations of the order parameter

$$\delta\sigma = \frac{e^{*2}}{m}\sum_k < |\psi(k)|^2 > \frac{\tau_{\mathbf{k}}}{2} \tag{6.9}$$

The equation obtained for the the conductivity has a Drude form , when $< |\psi(k)|^2 >$ is identified with the density of the superconductive fluctuating k mode and $\tau_{\mathbf{k}}/2$

with the relaxation time of the pair. Making the summation over the k in eq.(6.9), the fluctuation conductivity reads

$$\delta\sigma = \frac{e^{*2}}{\hbar}\frac{\tau_{LG}k_BT_c}{\hbar}\frac{1}{\xi^2(T)}\frac{1}{V}\sum_k \frac{1}{(\xi^{-2}(T)+k^2)^2}. \tag{6.10}$$

For a three dimensional sample we get

$$\begin{aligned}\delta\sigma_3 &= \frac{e^{*2}}{\hbar}\frac{\tau_{LG}k_BT_c}{\hbar}\frac{1}{\xi^2(T)}\frac{1}{2\pi^2}\int_0^{\xi^{-1}(T)} dk\frac{k^2}{(\xi^{-2}(T)+k^2)^2} = \\ &= \frac{1}{32}\frac{e^2}{\hbar\xi_0}\left(\frac{T_c}{T-T_c}\right)^{1/2}\end{aligned} \tag{6.11}$$

and

$$\begin{aligned}\delta\sigma_2 &== \frac{e^{*2}}{\hbar}\frac{\tau_{LG}k_BT_c}{\hbar}\frac{1}{\xi^2(T)}\frac{1}{4\pi d}\int_0^{\xi^{-2}(T)} dk^2\frac{1}{(\xi^{-2}(T)+k^2)^2} = \\ &= \frac{1}{32}\frac{e^2}{\hbar\xi_0}\left(\frac{2\xi(T)}{d}\right)\left(\frac{T_c}{T-T_c}\right)^{1/2}\end{aligned} \tag{6.12}$$

for a two dimensional system. This is the result first obtained by Azlamazov and Larkin [28]. Here d is the thickness of a quasi two-dimensional sample. In the last equality of eqs.(6.11) and (6.12) we have used for the the Landau-Ginzburg relaxation time (6.8) the value of the parameter ratio $\gamma/a' = \pi\hbar/8k_B$ as derived by microscopic theory in Appendix A and reported in eq.(7.52). In dirty samples $\xi_0 \to (l\xi_0)^{1/2}$ and the effect of the fluctuations in three dimensional systems is enhanced. To appreciate the magnitude of the correction due to fluctuations, we note that in the case of a three dimensional sample with the normal conductivity $\sigma_0 = ne^2\tau/m$, where τ is the scattering time of the normal electrons, we have

$$\delta\sigma_3/\sigma_0 \sim (1/k_F\xi_{0,c})(\hbar/E_F\tau)(T_c/(T-T_c))^{1/2} \sim (k_BT_c/E_F)(\hbar/E_F\tau)(T_c/(T-T_c))^{1/2}$$

for clean metals and

$$\delta\sigma_3/\sigma_0 \sim (k_BT_c/E_F)^{1/2}(\hbar/E_F\tau)^{3/2}(T_c/(T-T_c))^{1/2}$$