for dirty materials. In ordinary superconductors with $T_c \sim 10K$, $E_F \sim 1eV$, $\tau \sim 10^{-14}s$ and $\xi_0 \sim 2000\text{Å}$, this gives a ratio $\delta\sigma/\sigma_0 \sim 10^{-7}(T_c/(T-T_c))^{-1/2}$: $10^{-2}(T_c/(T-T_c))^{-1/2}$ ranging from clean to extremely dirty metals [25].

As shown by the second equality of eq.(6.12), the fluctuation effects are greatly enhanced in two dimensional samples by a factor $2\xi(T)/d$. The experiment by Glover [26] was in fact performed on a bismuth film.

In the case of high T_c superconductors the smallness of the zero temperature coherence distance $\xi_0 \sim 10\text{Å}$ makes more accessible the region where the deviations from the mean field theory [27] and the magnitude of the fluctuation correction are apreciable in three dimensional clean samples also. In this respect, measurements of the resistivity in $Y_1Ba_2Cu_3O_{9-\delta}$ high T_c superconductors [32] strongly suggest , near the transition, the relevance of superconductive fluctuations in agreement with the three dimensional expression derived by Aslamazov and Larkin [28].

7 THE MICROSCOPIC APPROACH

I) Hartree-Fock approximation

In the third section we established the basis for a microscopic theory for superconductivity. This has to reproduce the fundamental requirement of ODLRO in the two particle reduced density matrix and therefore the electrons have to be bound in pairs.

We recall that the one and two particle reduced density matrices in the second quantized formalism are written in terms of quantum statistical averages of products of creation and annihilation operators $\psi_\sigma^\dagger(\mathbf{x})$ and $\psi_\sigma(\mathbf{x})$

$$h_1(\mathbf{x}, \mathbf{x}') = < \psi_\sigma^\dagger(\mathbf{x}')\psi_\sigma(\mathbf{x}) > \tag{7.1}$$

$$h_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_2', \mathbf{x}_1') = < \psi_\sigma^\dagger(\mathbf{x}_1')\psi_\tau^\dagger(\mathbf{x}_2')\psi_\tau(\mathbf{x}_2)\psi_\sigma(\mathbf{x}_1) > \tag{7.2}$$

where the sum over repeated spin indices is understood.

A normal system with electrons with momentum $\mathbf{k}$ and spin σ can be approximated by a Slater determinant of Bloch functions, which in terms of creation oper-

ators in k space $a^\dagger_{k,\sigma}$ can be written as

$$|n> = \prod_{0<|k|<k_F} a^\dagger_{k,\uparrow} a^\dagger_{-k,\downarrow} |0> \qquad (7.3)$$

k_F being the Fermi momentum.

$\psi_\sigma(x)$ and $a_{k,\sigma}$ are related via the single particle wave functions $g_{k,\sigma}(x)$

$$\psi_\sigma(x) = \sum_k g_{k,\sigma}(x) a_{k,\sigma}. \qquad (7.4)$$

If we perform the average processes with respect to the state given by eq.(7.3), h_2 is factorized in terms of h_1 as for a free electron gas

$$h_2(x_1, x_2; x'_2, x'_1) = h_1(x_1, x'_1)h_1(x_2, x'_2) - h_1(x, x'_2)h_1(x_2, x'_1). \qquad (7.5)$$

This is equivalent to the Hartree-Fock approximation.

This expression of course does not show ODLRO, since h_1 cannot have macroscopic eigenvalues According to its definition (3.20), ODLRO is present if we can construct a ground state $|s>$ which yields a generalized Hartree-Fock approximation such that

$$h_2(x_1, x_2; x'_2, x'_1) = h_1(x_1, x'_1)h_1(x_2, x'_2) - h_1(x, x'_2)h_1(x_2, x'_1) +$$

$$+ \chi^*(x'_1, x'_2)\chi(x_1, x_2) \qquad (7.6)$$

where χ has the meaning of the pair wave function. Bardeen Cooper and Schrieffer have accomplished this task [14].

We shall now study their microscopic theory following the generalized Hartree-Fock approach in the matrix form introduced by J.G.Valatin [33].

We start by considering the usual Hartree-Fock approximation for a normal metal. It is essentially a variational method whose aim is to reach by means of an effective field the best single particle "description" of a system of interacting particles.

The Hamiltonian is formed by a two body interaction and a single particle energy scaled to the chemical potential λ in the second quantized representation:

$$H = \int dx \int dx' \psi_\sigma^\dagger(x)\epsilon(x,x')\psi_\sigma(x') + \frac{1}{2}\int dx \int dx' \psi_\sigma^\dagger(x)\psi_\tau^\dagger(x')V(x,x')\psi_\tau(x')\psi_\sigma(x).$$

(7.7)

where

$$\epsilon(x,x') = \left(-\frac{\hbar^2}{2m}\nabla^2 - \lambda\right)\delta(x-x')$$

(7.8)

The Hartree-Fock approximation amounts to factor the expectation value of the quadrilinear term into the product of two bilinear terms according to eq.(7.5). At zero temperature the ground state energy is

$$W_0 = <n|H|n> = \int dx \int dx'\epsilon(x,x')h_1(x',x) + \frac{1}{2}\int dx \int dx'U(x,x')h_1(x',x) =$$

$$= \frac{1}{2}Tr\left(\epsilon h_1 + \nu h_1\right)$$

(7.9)

where the single particle energy ν contains the Hartree-Fock self-potential U

$$\nu(x,x') = \epsilon(x,x') + U(x,x'),$$

$$U(x,x') = \delta(x-x')\int dy V(x-y)h_1(y,y) - V(x-x')h_1(x,x').$$

(7.10)

The second equality of eq.(7.9) is written in matrix notation and the potential V is assumed to depend on $x-x'$ only. In the same approximation the single particle reduced density matrix becomes

$$h_1(x,x') = \sum_{|k|<k_F} n_{k,\sigma} g_{k,\sigma}^*(x') g_{k,\sigma}(x)$$

(7.11)

where

$$n_{k,\sigma} = <n|a_{k,\sigma}^\dagger a_{k,\sigma}|n>.$$

(7.12)

So that in matrix notation

$$h_1^2 = h_1.$$

(7.13)

By minimizing the ground state energy W_0 with the constraint (7.13) and introducing the Lagrangian multiplier η one has

$$\delta W_0 - \delta\left(Tr\eta\left[h_1 - h_1^2\right]\right) = 0$$

(7.14)

with

$$\delta W_0 = Tr\nu\delta h_1 = \int dx \int dx'\nu(\mathbf{x},\mathbf{x}')\delta h_1(\mathbf{x}',\mathbf{x}). \qquad (7.15)$$

By exploiting the cyclic permutation in eq.(7.14) under the trace we obtain

$$\nu - \eta + \eta h_1 + h_1\eta = 0.$$

The property (7.13) then gives rise to the Hartree-Fock equation [33] in the matrix form:

$$[\nu, h_1] = 0. \qquad (7.16)$$

The connection with the usual form of the Hartree-Fock equation can be found in ref. [33].

Whithin the approximation considered, according to eq.(7.15) the variation of energy from the ground state due to a variation of h_1 is characterised by what we have called single particle energy ν. We can therefore, approximate the quadrilinear Hamiltonian (7.7) by the following bilinear expression

$$H \sim H_0 = const + \int dx \int dx'\psi_\sigma^\dagger(\mathbf{x})\nu(\mathbf{x},\mathbf{x}')\psi_\sigma(\mathbf{x}') = const + \sum_{\mathbf{k},\sigma} \nu_\mathbf{k} a_{\mathbf{k},\sigma}^\dagger a_{\mathbf{k},\sigma}. \quad (7.17)$$

It has been assumed that

$$\nu_{\mathbf{k},\mathbf{k}'} = \int dx \int dx' g_{\mathbf{k}',\sigma}^*(\mathbf{x})\nu(\mathbf{x},\mathbf{x}')g_{\mathbf{k},\sigma}(\mathbf{x}') \qquad (7.18)$$

is diagonal, as it can always be done by a proper choice of the single particle states. ν acquires the meaning of single particle excitations from the ground state or "quasi-particles". H_0 can be obtained from H by a linearization procedure in which couples of operators $\psi_\sigma^\dagger(\mathbf{x})$ and $\psi_\sigma(\mathbf{x}')$ are substituted by their averaged value (7.11).

At $T \neq 0$ the same equation (7.15) is valid provided we consider $h_1 = <\psi^\dagger\psi>$ as obtained by a quantum statistical average over a restricted ensemble with statistical operator

$$U = e^{-\beta H} \qquad (7.19)$$

expressed in term of the approximate Hamiltonian (7.17).

When we consider time-dependent phenomena as for example transport properties it is necessary to know the behaviour of the density matrix h_1 as a function of time. In order to generalize the Hartree-Fock equation to the time dependent case, we use the decomposition of h_1 in terms of single particle time dependent wave functions

$$h_1(x, x', t) = \sum_{k,\sigma} n_{k,\sigma} g^*_{k,\sigma}(x', t) g_{k,\sigma}(x, t). \qquad (7.20)$$

Using the equation of motion for the single particle wave functions we get the time-dependent Hartree-Fock equation in the matrix form [33]

$$i\hbar \frac{\partial h_1}{\partial t} = [\nu, h_1]. \qquad (7.21)$$

When the temperature is becoming higher and higher too many quasiparticles are statistically excited so that they start interacting with one another. The previous scheme of approximation loses its validity. Owing to the reciprocal scattering, the quasiparticles have such a short life-time that their concept itself looses its validity.

II) The theory of Bardeen Cooper and Schrieffer

a)The ground state

In superconductivity because of pair formation, eq.(7.16) is not adequate. We shall generalize the matrix expression of the equation of motion in a form suitable to the present case. Factorization procedure has to occur according to equation (7.6) rather than according to eq.(7.5).

In order for the superconductivity phase to be stable with respect to the normal phase, the ground state , the state $|s>$ we are looking for, must lead to a lower energy than that of the ground state for the normal system $|n>$. Because of the isotope effect the interaction leading to superconductivity, at least for most of the elements, must be due to phonons. The effective electron-electron interaction via phonons is weak and attractive i.e. negative in a region around the Fermi surface and it has not been included in the Bloch states which approximate the normal electron states. Because of this interaction, pairs of electrons will be scattered from states k_1 and k_2 to states k'_1 and k'_2 with momentum conservation. Even though

the potential is negative, the matrix elements of the potential between different spin configurations can be either positive or negative depending on the number of transpositions of indices we have to make on the ordered state to calculate these matrix elements. Statistically therefore, even with an attractive potential, we would have a zero mean energy gain with respect to the normal case. We have therefore to choose a subset of configurations such as to allow the potential matrix elements to remain negative. If the states are occupied by pairs of electrons in the sense that if one is occupied another related to it must be also occupied, then the number of transpositions is always even and we have fulfilled our task. These pairs must have the same momentum so that the number of allowed collisions is minimum and the energy gain is maximum. Of course if there is no net flow this momentum must be zero. We have reached again the point discussed in the third section i.e. the superconductive state must be formed by bound pairs of electrons with opposite momentum k and spin σ. The ground state $|s>$ is therefore a coherent mixing of Bloch states occupied in pairs.

A normalized state satisfying all the requirements discussed above and leading to eq.(7.6) is given by

$$|s> = \prod_{0<|k|<k_F} \left((1 - h_k)^{1/2} + (h_k)^{1/2} a^{\dagger}_{k,\uparrow} a^{\dagger}_{-k,\downarrow} \right) |0> .$$ (7.22)

In the absence of an external field and for the homogenous systems, the single particle states are momentum states as we have said. In the general case the best choice of single particle states $g_k(x)$ has to be determined by variational principle.

The state written above does not conserve the total number of particles. There is in fact a probability different from zero for any number of pairs. This difficulty of the formalism could be avoided by projecting on a N particle state . Because of the large number of particles , however, no essential errors are introduced if we impose that the averaged number of particles is equal to the total number N. This introduces a constraint on the parameters h_k and through them on the chemical potential λ.

Let us check that what we have written as $h_{\mathbf{k}}$ really corresponds to the occupation number i.e. to the k space representation of the single particle density matrix. In fact

$$h_{\mathbf{k,k'}} = < s|a_{\mathbf{k},\sigma}^{\dagger} a_{\mathbf{k'},\sigma}|s > = h_{\mathbf{k}}\delta_{\mathbf{k,k'}} \qquad (7.23)$$

$$h_1(\mathbf{x},\mathbf{x'}) = < s|\psi_{\sigma}^{\dagger}(\mathbf{x'})\psi_{\sigma}(\mathbf{x})|s > = \sum_{\mathbf{k}} h_{\mathbf{k}} g_{\mathbf{k},\sigma}^*(\mathbf{x'}) g_{\mathbf{k},\sigma}(\mathbf{x}). \qquad (7.24)$$

Together with $h_{\mathbf{k}} = n_{\mathbf{k}} = h_{-\mathbf{k}}$, we have to define the new quantity

$$\chi_{\mathbf{k'},\downarrow,\mathbf{k},\uparrow} = < s|a_{\mathbf{k'},\downarrow} a_{\mathbf{k},\uparrow}|s > = (h_{\mathbf{k}})^{1/2}(1-h_{\mathbf{k'}})^{1/2}\delta_{\mathbf{k,-k'}} = \chi_{\mathbf{k}}\delta_{\mathbf{k,-k'}}, \qquad (7.25)$$

$$\chi_{\mathbf{k},\uparrow,\mathbf{k'},\downarrow} = -\chi_{\mathbf{k}}\delta_{\mathbf{k,-k'}}$$

$$\chi(\mathbf{x},\mathbf{x'}) = < s|\psi_{\downarrow}(\mathbf{x'})\psi_{\uparrow}(\mathbf{x})|s > = \sum_{\mathbf{k}} \chi_{\mathbf{k}} g_{\mathbf{k},\uparrow}(\mathbf{x}) g_{-\mathbf{k},\downarrow}(\mathbf{x'}). \qquad (7.26)$$

$\chi_{\mathbf{k}}$ coincides with the k representation of the pair wave function. In fact the expectation value of h_2 leads to eq.(7.6), with χ defined according to eq.(7.25) and eq.(7.26). We have the new constraint

$$(1-2h_{-\mathbf{k}})(1-2h_{\mathbf{k}}) + (2\chi_{\mathbf{k}})^2 = 1. \qquad (7.27)$$

b)The quasi-particle excitations and ODLRO

Because of the pair wave function, we have, in addition to the self-potential U given by eq.(7.10), the pair potential

$$\mu(\mathbf{x},\mathbf{x'}) = V(\mathbf{x}-\mathbf{x'})\chi(\mathbf{x},\mathbf{x'}), \qquad (7.28)$$

or in k space

$$\mu_{\mathbf{k,k'}} = \int d\mathbf{x} \int d\mathbf{x'} g_{\mathbf{k}}^*(\mathbf{x})\mu(\mathbf{x},\mathbf{x'}) g_{\mathbf{k}}^*(\mathbf{x'}) =$$

$$= \mu_{\mathbf{k}}\delta_{\mathbf{k,-k'}} = \sum_{\mathbf{k''}} V_{\mathbf{k}\uparrow,-\mathbf{k}\downarrow;\mathbf{k''}\uparrow,-\mathbf{k''}\downarrow}\chi_{\mathbf{k''}}\delta_{\mathbf{k,-k'}}. \qquad (7.29)$$

The integral of eq.(7.28) with respect to the relative coordinate $\mathbf{x}-\mathbf{x'}$ gives Gor'kov's order parameter (3.23). This quantity appears in both the new ground state energy W_0 and the new linearised hamiltonian H_0 , which we have to write in the place of eq. (7.9) and eq.(7.17) respectively. The ground state energy reads:

$$W_0 = < s|H|s > = \frac{1}{2} \int d\mathbf{x} \int d\mathbf{x'}\epsilon(\mathbf{x},\mathbf{x'})h_1(\mathbf{x'},\mathbf{x}) + \frac{1}{2} \int d\mathbf{x} \int d\mathbf{x'}\nu(\mathbf{x},\mathbf{x'})h_1(\mathbf{x'},\mathbf{x})$$

$$+ \frac{1}{2} \int dx \int dx' \mu^*(x,x')\chi(x',x) = \frac{1}{2}\sum_{\mathbf{k}}((\epsilon_{\mathbf{k}}+\nu_{\mathbf{k}})h_{\mathbf{k}}+\mu_{\mathbf{k}}\chi_{\mathbf{k}}) \qquad (7.30)$$

or in matrix notations

$$W_0 = \frac{1}{2}Tr\left(\epsilon h_1 + \nu h_1 + \mu^*\chi\right). \qquad (7.31)$$

Variation of W_0 with respect to h and χ under constraint given by eq.(7.27) leads in the k-space representation to

$$\nu_{\mathbf{k}}\delta h_{\mathbf{k}} + \mu_{\mathbf{k}}\delta\chi_{\mathbf{k}} + E_{\mathbf{k}}\left(2\chi_{\mathbf{k}}\delta\chi_{\mathbf{k}} - (1-2h_{\mathbf{k}})\delta h_{\mathbf{k}}\right) = 0 \qquad (7.32)$$

where $E_{\mathbf{k}}$ is a Lagrangian multiplier.

Solutions of the above equations are

$$h_{\mathbf{k}} = \frac{1}{2}\left(1 - \frac{\nu_{\mathbf{k}}}{E_{\mathbf{k}}}\right) \qquad \chi_{\mathbf{k}} = -\frac{1}{2}\frac{\mu_{\mathbf{k}}}{E_{\mathbf{k}}} \qquad (7.33)$$

and

$$E_{\mathbf{k}} = \left(\nu_{\mathbf{k}}^2 + \mu_{\mathbf{k}}^2\right)^{1/2}. \qquad (7.34)$$

According to eqs.(7.23),(7.24) and (7.25),(7.26) the linearization procedure of the Hamiltonian we have carried out to get the excitation Hamiltonian valid in the normal case, leads now to an expression which contains both h_1 and χ and therefore ν and μ

$$H_0 = const + \sum_{\mathbf{k},\sigma}\nu_{\mathbf{k}}a_{\mathbf{k},\sigma}^\dagger a_{\mathbf{k},\sigma} + \frac{1}{2}\sum_{\mathbf{k}}\mu_{\mathbf{k}}\left(a_{\mathbf{k},\uparrow}^\dagger a_{-\mathbf{k},\downarrow}^\dagger + a_{-\mathbf{k},\downarrow}a_{\mathbf{k},\uparrow}\right). \qquad (7.35)$$

This expression is clearly non diagonal and we have therefore to introduce a canonical transformation in order to diagonalize it. New operators $\xi_{\mathbf{k},\sigma}$ and $\xi_{\mathbf{k},\sigma}^\dagger$ have to be introduced satisfying the same anticommutation rules as $a_{\mathbf{k},\sigma}$ and $a_{\mathbf{k},\sigma}^\dagger$. The famous Bogolubov-Valatin transformation [33, 34, 35] is

$$\xi_{\mathbf{k},\sigma} = (1-h_{\mathbf{k}})^{1/2}a_{\mathbf{k},\sigma} - \sigma(h_{\mathbf{k}})^{1/2}a_{-\mathbf{k},-\sigma}^\dagger \qquad (7.36)$$

$$\xi_{\mathbf{k},\sigma}^\dagger = (1-h_{\mathbf{k}})^{1/2}a_{\mathbf{k},\sigma}^\dagger - \sigma(h_{\mathbf{k}})^{1/2}a_{-\mathbf{k},-\sigma} \qquad (7.37)$$

The ground state $|s>$ given by eq.(7.22) is the vacuum state for the operators ζ i.e. $\zeta_{\mathbf{k}}|s>= 0$ for any k.

Provided $h_{\mathbf{k}}$ is given by eq.(7.33) after transformation , the Hamiltonian (7.35) reduces to

$$H_0 = W_0 + \sum_{\mathbf{k},\sigma} E_{\mathbf{k}} \zeta_{\mathbf{k},\sigma}^{\dagger} \zeta_{\mathbf{k},\sigma}. \tag{7.38}$$

Here $E_{\mathbf{k}}$ is the new quasiparticle energy.

Let us take for simplicity a model in which the Hartree-Fock self-potential U is zero and the potential V can be assumed as a constant in a region $2\omega_D$ around the Fermi surface, ω_D being the Debye frequency

$$V_{\mathbf{k}\uparrow,-\mathbf{k}\downarrow;\mathbf{k}'\uparrow,-\mathbf{k}'\downarrow} = -V \qquad -\omega_D \le \epsilon_{\mathbf{k}}, \epsilon_{\mathbf{k}'} \le \omega_D$$

$$V_{\mathbf{k}\uparrow,-\mathbf{k}\downarrow;\mathbf{k}'\uparrow,-\mathbf{k}'\downarrow} = 0 \qquad otherwise \tag{7.39}$$

as in the B.C.S. original paper.

The pair wave function in the k representation is spin independent i.e. in the bulk superconductors $\chi_{-\mathbf{k}\downarrow,\mathbf{k}\uparrow} = \chi_{\mathbf{k}}$ and the pair potential $\mu_{\mathbf{k}}$ reduces to a constant Δ, Δ being the gap energy appearing in the quasiparticle spectrum. In fact from eqs.(7.29) and (7.33) we have

$$\Delta = \mu_{\mathbf{k}} = V \sum_{\mathbf{k}'} \frac{\mu_{\mathbf{k}'}}{2E_{\mathbf{k}'}} = V\Delta \sum_{\mathbf{k}'} \frac{1}{2E_{\mathbf{k}'}}, \qquad |\epsilon_{\mathbf{k}}| \le \omega_D$$

$$\Delta = 0 \qquad otherwise, \tag{7.40}$$

ω_D is much smaller than the Fermi energy and the density of state in the shell $2\omega_D$ around the Fermi surface can be considered constant. Equation for Δ then reads:

$$\frac{1}{N_0 V} = \int_0^{\omega_D} \frac{d\epsilon}{(\epsilon^2 + \Delta^2)^{1/2}} = sh^{-1}\left(\frac{\omega_D}{\Delta}\right), \tag{7.41}$$

where N_0 is the single particle density of states at the Fermi energy. For most superconductors $N_0 V \ll 1$ and we get

$$\Delta \sim 2\omega_D e^{-1/N_0 V}. \tag{7.42}$$

The Debye frequency ω_D present in the last equation accounts for the isotope effect.

Solution (7.41) is clearly non perturbative. This is the reason for the difficulty in explaining superconductivity i.e. superconductive behavior cannot be obtained by any perturbative expansion from the normal state. In fact we had to imagine a completely new state. We were guided by many considerations, among them the factorization property (7.6) for h_2 in order to have condensation. Bardeen, Cooper and Schrieffer at $T = 0$ have calculated within their model the behavior of the functions $\phi(r) = 1/(\alpha N)^{1/2}\chi(r)$ appearing in eq.(3.20). It turns out

$$\lim_{r=|x_1-x_2|\to\infty} \phi^{BCS}(r) = \lim_{r=|x_1-x_2|\to\infty} \frac{1}{(\alpha N)^{1/2}}\chi(r) =$$

$$= \frac{C}{(\Omega)^{1/2}} \left[\frac{1}{r}K_0\left(\frac{r}{\pi\xi_0}\right) + \frac{\Delta}{\omega_D}\frac{\pi\xi_0}{r^2}sin\left(\frac{\omega_D r}{\Delta\pi\xi_0}\right)\right]. \qquad (7.43)$$

K_0 is the modified Bessel function with an asymptotic exponential decrease. The second term proportional to $1/r^2$ is usually neglected because of the smallness of the ratio Δ/ω_D. However we stated that ODLRO automatically leads to condensation for the restricted class of functions sensibly different from zero in a finite region of r.

So that even in B.C.S. theory in order to show the state $|s >$ given eq.(7.22) leads to condensation we have to solve explicitly the eigenvalue equation for the two particle reduced density matrix h_2 given by eq.(7.6) , considering explicitly the B.C.S. solution (7.33) for h and χ [13].

Fourier transforming the eigenvalue equation

$$\int dx_1' \int dx_2' h_2(x_1, x_2, x_2', x_1')\phi_i(x_1', x_2') = \lambda_i\phi_i(x_1, x_2) \qquad (7.44)$$

and using the explicit B.C.S. expression (7.6) and (7.33) ,we obtain

$$h_k^2(\phi(k) + \phi(-k)) + \sum_{k'} \phi(k')\chi_{k'}^*\chi_k = \lambda\phi(k) \qquad (7.45)$$

or remembering that $\phi(k) = \phi(-k)$, we have

$$\sum_{k'} \phi(k')\frac{\chi_{k'}^*\chi_k}{\lambda - 2h_k^2} = \phi(k), \qquad (7.46)$$

which reduces to

$$1 = \sum_{\mathbf{k}} \frac{|\chi_{\mathbf{k}}|^2}{\lambda - 2h_{\mathbf{k}}^2}. \qquad (7.47)$$

From equation (7.33) it turns out that

$$\lim_{N \to \infty} \sum_{\mathbf{k}} |\chi_{\mathbf{k}}|^2 = \frac{\Omega}{(2\pi)^3} \int d^3k |\chi_{\mathbf{k}}|^2 = \alpha N \qquad (7.48)$$

with finite α.

$h_{\mathbf{k}}$ is the microscopic occupation number of the state k and is therefore negligible as compared to N in the limit of $N \to \infty$. In this limit (7.45) admits an eigenvalue

$$\lambda = \sum_{\mathbf{k}} |\chi_{\mathbf{k}}|^2 = \alpha N \qquad (7.49)$$

and in the same limit no other isolated eigenvalue exist. As suggested in the third section the eigenfunction corresponding to this maximum eigenvalue is from eq.(7.43)

$$\phi(\mathbf{k}) = \frac{1}{(\alpha N)^{1/2}} \chi_{\mathbf{k}} \qquad (7.50)$$

i.e. it coincides but for the factor $(\alpha N)^{1/2}$ with the function which characterised the ODLRO property of h_2 as in eq.(3.20).

In so far we have discussed the B.C.S. microscopic theory for superconductivity at zero temperature. In the remaining of this section we shall briefly sketch how to extend this result at finite temperature referring for a detailed derivation to the original paper of Bardeen, Cooper and Schriffer [14] or to the references [33, 36].

As we have seen the ground state $|s>$ is the vacuum state for the quasiparticles defined by the Bogolubov-Valatin transformations defined in eqs.(7.36),(7.37) with the Hamiltonian given by eq.(7.38). At $T = 0$ no quasiparticles are present so that the quasiparticle number operator applied to the fundamental B.C.S. state is zero. At $T \neq 0$ however the quasiparticles being fermions will satisfy the Fermi statistics i.e.

$$f_{\mathbf{k}} = < \xi_{\mathbf{k},\sigma}^{\dagger} \xi_{\mathbf{k}\sigma} > = \left(1 + e^{\beta E_{\mathbf{k}}}\right)^{-1}$$

where the average is a quantum statistical average and no sum over spin indices is here understood. Furthermore we shall indicate whenever necessary the quantities at $T \neq 0$ with a bar.

The new quasiparticle energies $\bar{E}_k$ have the same expression of the eq.(7.34) with the self-potential $\bar{\nu}$ and $\bar{\mu}$. $\bar{\nu}$ and $\bar{\mu}$ are obtained from the definition (7.10) and (7.28) of ν and μ. The temperature dependent $\bar{h}$ and $\bar{\chi}$ appear in place of h and χ respectively and it is easy to show that

$$(1 - 2\bar{h}_k) = (1 - 2h_k)(1 - 2f_k)$$

and

$$\bar{\chi}_k = \chi_k(1 - 2f_k).$$

The entropy of a Fermi gas of quasiparticles is known in terms of their occupation number f_k. So the free energy is $F = \bar{W}_0 - TS_0$. In the present case the solution of the problem at $T \neq 0$ is obtained by minimizing the free energy with respect to h_k , χ_k and f_k with the constraint eq.(7.27).

Under the hypothesis of eq.(7.39) and assuming the Hartree-Fock potential $\bar{U} = 0$, the gap equation reads

$$\frac{1}{N_0 V} = \int_0^{\omega_D} \frac{d\epsilon}{\left(\epsilon^2 + \bar{\Delta}^2\right)^{1/2}} th\left(\frac{1}{2}\beta \bar{E}_k\right). \qquad (7.51)$$

Near the critical temperature at which the gap energy vanishes [14], the explicit behavior of $\bar{\Delta}$ as a function of the temperature is

$$\bar{\Delta} \sim |T - T_c|^{1/2}$$

as derived but for a normalization factor from the Landau-Ginzburg equation. A specific heat jump as given by eq.(5.12) is also obtained [14].

The results obtained so far make clear that we can establish a direct connection between the phenomenological Landau-Ginzburg theory and the generalized Hartree-Fock type of approach. In the Appendix A we show that the time dependent Landau-Ginzburg equation (6.2) for the order parameter can be derived from the microscopic theory on the assumption of being near the critical temperature where the magnitude of the order parameter is small. Small space and time variations of

the order parameter are also considered. Here we report the microscopic expressions obtained in the appendix for the coefficients which appear in the phenomenological Landau-Ginzburg theory

$$a' = \frac{\hbar^2}{2mL^2T_c}, \quad b = B\left(\frac{T_c a'}{N_0}\right)^2, \quad \gamma = G\frac{T_c a'}{N_0}. \tag{7.52}$$

where

$$B = N_0\frac{7\zeta(3)}{8(\pi k_B T_c)^2}, \quad G = \frac{N_0\pi\hbar}{8k_B T_c}, \tag{7.53}$$

and L^2 is

$$L^2 = \frac{\hbar^2}{2m}\frac{7\zeta(3)E_F}{12(\pi k_B T_c)^2} \tag{7.54}$$

for clean metals and

$$L^2 = \frac{\pi\hbar}{24}\frac{v_F^2\tau}{k_B T_c} \tag{7.55}$$

for dirty superconductors. $\zeta(x)$ is the Riemann zeta function.

Recalling the eq.(5.26) for the zero temperature coherence distance ξ_0 we obtain in both limits (clean and dirty)

$$\xi_0^2 = \frac{c}{2a'T_c} = \frac{L^2}{2} \tag{7.56}$$

We find here, as one could have expected from the qualitative argument given at the end of section 5, that in going from the dirty to the clean case one has to make the substitution $D \sim (p_F l/m) \sim (E_F\tau/m) \to (E_F/m)(\hbar/k_B T_c)$.

The expression for the Landau-Ginzburg relaxation time reads

$$\tau_{LG}^{-1} = \frac{a}{\gamma} = \frac{8k_B}{\pi\hbar}(T - T_c) \tag{7.57}$$

and the specific heat jump of eq.(5.12) becomes

$$\Delta C = \frac{a'^2 T_c}{b} = \frac{8N_0\pi^2 k_B^2 T_c}{7\zeta(3)} = \frac{12}{7\zeta(3)}C_n = 1.43C_n \tag{7.58}$$

C_n being the the specific heat in the normal phase at T_c.

We have in this way completed our excursion from phenomenology to microscopic theory and back to phenomenology, having been guided by the condensation criterion and its consequences which are transparent in the density matrix approach.

Appendix A MICROSCOPIC DERIVATION OF THE
TIME-DEPENDENT LANDAU-GINZBURG EQUATIONS

A derivation of the Landau-Ginzburg equation from microscopic theory was given by Gor'kov [15] for pure materials and alloys. Gor'kov's derivation is valid near the critical temperature where the magnitude of the order parameter Δ is small. Spatial variations of the order parameter and of the external fields are also small.

The time dependent Landau-Ginzburg equation has been derived in many different ways essentially by means of the Green functions technique [37, 38]. An extension which includes the effects of the lattice vibrations on the relaxation rate of the order parameter has been also tried [39, 40] and the case of alloys with paramagnetic impurities has been considered in reference [41]. A complex analysis of the different regions of validity of a time dependent differential equation for the order parameter is given in references [42, 38]. The full discussion of this problem cannot be reported here.

In order to be as simple as possible we report the derivation given in reference [29] where the density matrix approach [33] so far considered, is used.

The behavior of a superconductor has been described in terms of the two quantities $h(\mathbf{x}, \mathbf{x}', t)$, $\chi(\mathbf{x}, \mathbf{x}', t)$. h is the one particle reduced density matrix and its diagonal elements give the electron density, while χ is the normalized eigenfunction of the two particle reduced density matrix and represents the wave function of the paired electrons in the condensate. No spatial inhomogeneity is allowed as long as h and χ are in the diagonal form (7.23)and (7.25) in k space. We have to generalize these equations to include spatial variations. At $T = 0$ we can write a generalized density matrix K [33] in the quasi particle space generated by the transformation

(7.36)and (7.37) to take into account the pair wave function χ

$$K = \begin{pmatrix} h_k & 0 & 0 & \chi_k \\ 0 & h_k & -\chi_k & 0 \\ 0 & -\chi_k & 1-h_k & 0 \\ \chi_k & 0 & 0 & 1-h_k \end{pmatrix} = \begin{pmatrix} h & \chi \\ -\chi^* & 1-h^* \end{pmatrix}. \qquad (A.1)$$

The equations of motion for the generalized density matrix K are determined by a generalized "single particle energy" which includes the pair potential and is given by the matrix M

$$M = \begin{pmatrix} \nu_k & 0 & 0 & \mu_k \\ 0 & \nu_k & -\mu_k & 0 \\ 0 & -\mu_k & -\nu_k & 0 \\ \mu_k & 0 & 0 & -\nu_k \end{pmatrix} = \begin{pmatrix} \nu & \mu \\ -\mu^* & -\nu^* \end{pmatrix} \qquad (A.2)$$

where $\nu(\mathbf{x},\mathbf{x}')$ is the self-consistent single particle Hartree-Fock Hamiltonian and $\mu(\mathbf{x},\mathbf{x}',t)$ is the self-consistent pair potential (7.28) which is related to the Landau order parameter. Of course in the case presented above the transformations (7.36),(7.37) diagonalise M, which commutes with K

$$[M,K] = 0 \qquad (A.3)$$

and because of eq.(7.27)

$$K^2 = K. \qquad (A.4)$$

Equations (A.3) and (A.4) are the direct generalization of the Hartree-Fock equations (7.16) and (7.13). In the case of inhomogenous system h and χ are no more diagonal in k space and the Bogolubov-Valatin transformation must be generalised to include coefficient depending both on $\mathbf{k}$ and $\mathbf{k}'$. The explicit representation given by the first matrix of eq.(A.1) and eq.(A.2) is no more valid. These equations however are still valid provided h, χ, ν and μ are matrices with off-diagonal elements.

The equation of motion for K within the generalized Hartree-Fock approximation is then

$$i\hbar \frac{\partial K}{\partial t} = [M,K]. \qquad (A.5)$$

Eq.(A.5) is the straightforward generalization of eq.(7.21). The approximation underlying eq.(A.5) is the factorization property (7.6) of the two-particle reduced density matrix h_2. Eq.(A.5) is also obtained at finite temperature provided all the quantities here considered are the quantum statistical averages $\bar{h}, \bar{\chi}, \bar{\nu}$ and $\bar{\mu}$ necessary to define the temperature dependent $\bar{K}$ and $\bar{M}$.

In order to solve this equation in the general case of space and time variation of the order parameter, we shall set up a perturbative approach.

Our purpose is to derive an equation describing the time and spatial variation of the order parameter and the related density and current variations. The last two quantities are known once the one-particle density matrix h is known. The self consistency requirement (7.28) tells us how to build the order parameter Δ once $\bar{\chi}$ is known. All the physical quantities we are interested in are therefore obtained once we know how to calculate the matrix $\bar{K}$ at all orders with respect to a fictitious external source

$$\bar{M}_e^1 = \begin{pmatrix} 0 & \delta\bar{\mu}(\mathbf{x}, t) \\ -\delta\bar{\mu}^*(\mathbf{x}, t) & 0 \end{pmatrix}. \tag{A.6}$$

The zeroth order solution is supposed to be time-independent and known, i.e. the matrices $\bar{M}^{(0)}$ and $\bar{K}^{(0)}$ are such that

$$\left[\bar{M}^{(0)}, \bar{K}^{(0)}\right] = 0.$$

At the various orders we have:

$$i\hbar\frac{\partial \bar{K}^{(1)}(t)}{\partial t} = \left[\bar{M}^{(0)}, \bar{K}^{(1)}\right] + \left[\bar{M}_e^{(1)}, \bar{K}^{(0)}\right] + \left[\bar{M}(\bar{K}^{(1)}), \bar{K}^{(0)}\right]$$

$$i\hbar\frac{\partial \bar{K}^{(2)}(t)}{\partial t} = \left[\bar{M}^{(0)}, \bar{K}^{(2)}\right] + \left[\bar{M}_e^{(1)}, \bar{K}^{(1)}\right] + \left[\bar{M}(\bar{K}^{(1)}), \bar{K}^{(1)}\right] + \left[\bar{M}(\bar{K}^{(2)}), \bar{K}^{(0)}\right]$$

$$i\hbar\frac{\partial \bar{K}^{(3)}(t)}{\partial t} = \left[\bar{M}^{(0)}, \bar{K}^{(3)}\right] + \left[\bar{M}_e^{(1)}, \bar{K}^{(2)}\right] + \left[\bar{M}(\bar{K}^{(1)}), \bar{K}^{(2)}\right] + \left[\bar{M}(\bar{K}^{(2)}), \bar{K}^{(1)}\right] + \left[\bar{M}(\bar{K}^{(3)}), \bar{K}^{(0)}\right]$$

$$\ldots = \ldots$$

The various $\bar{M}(\bar{K}^{(i)})$ come from the fact that the self-potentials $\bar{U}^{(i)}$ and $\bar{\mu}^{(i)}$ appearing in $\bar{M}$ are related to the $\bar{h}^{(i)}$ and $\bar{\chi}^{(i)}$ and therefore to $\bar{K}^{(i)}$ through the self-consistency relations.

Rearranging the preceding equations we obtain

$$i\hbar\frac{\partial \bar{K}(t)}{\partial t} = \left[\bar{M}^{(0)}, \bar{K}^{(1)} + \bar{K}^{(2)} + \bar{K}^{(3)} + ...\right] +$$

$$\left[\bar{M}_e^{(1)} + \bar{M}(\bar{K}^{(1)}) + \bar{M}(\bar{K}^{(2)}) + ..., \bar{K}^{(0)}\right] +$$

$$\left[\bar{M}_e^{(1)} + \bar{M}(\bar{K}^{(1)}) + \bar{M}(\bar{K}^{(2)}) + ..., \bar{K}^{(1)}\right] + ... = 0$$

We define a new $\bar{M}^{(1)} = \bar{M}_e^{(1)} + \bar{M}(\bar{K}^{(1)}) + \bar{M}(\bar{K}^{(2)}) + ...$ and find that the zeroth order equation is not changed whereas at the n-th order we have

$$i\hbar\frac{\partial \bar{K}^{(n)}(t)}{\partial t} = \left[\bar{M}^{(0)}, \bar{K}^{(n)}(t)\right] + \left[\bar{M}^{(1)}(t), \bar{K}^{(n-1)}(t)\right]. \qquad (A.7)$$

Eq.(A.7) is very suitable for the self-consistent calculation we are performing. Due to the self consistency conditions each term contains corrections at any order.

The formal solution of eq.(A.7) can be put in the following form

$$\bar{K}^{(n)}(t) = -\frac{i}{\hbar}\int_{-\infty}^{t} dt' e^{-i\bar{M}(0)(t-t')/\hbar} \left[\bar{M}^{(1)}(t'), \bar{K}^{(n-1)}(t')\right] e^{i\bar{M}(0)(t-t')/\hbar} \qquad (A.8)$$

as it can be seen by differentiation.

From now onwards to avoid unnecessary complications we shall always consider the Hartree-Fock self-potential $\bar{U}$ equal to zero.

Eq.(A.8) becomes easy to handle if $\bar{M}^{(0)}$ appearing in the exponential is in a diagonal representation. In the general case we have therefore to work in the quasiparticle space obtained by means of the Bogolubov-Valatin transformation. At $T \neq 0$ these transformations bring $\bar{M}^{(0)}$ into the diagonal form

$$\tilde{M}^{(0)} = U\bar{M}^{(0)}U^{-1} = \begin{pmatrix} \bar{E}_{\mathbf{k}} & 0 & 0 & 0 \\ 0 & \bar{E}_{\mathbf{k}} & 0 & 0 \\ 0 & 0 & -\bar{E}_{\mathbf{k}} & 0 \\ 0 & 0 & 0 & -\bar{E}_{\mathbf{k}} \end{pmatrix},$$

$$\tilde{K}^{(0)} = U \bar{K}^{(0)} U^{-1} = \begin{pmatrix} f_\mathbf{k} & 0 & 0 & 0 \\ 0 & f_\mathbf{k} & 0 & 0 \\ 0 & 0 & 1-f_\mathbf{k} & 0 \\ 0 & 0 & 0 & 1-f_\mathbf{k} \end{pmatrix},$$

where $f_\mathbf{k}$ is the Fermi quasi-particle distribution.

In the transformed quasiparticle space the solution of the time dependent equation of motion is still of the form (A.8)

$$\tilde{K}^{(n)}(t) = -\frac{i}{\hbar} \int_{-\infty}^{t} dt' e^{-i\tilde{M}^{(0)}(t-t')/\hbar} \left[\tilde{M}^{(1)}(t'), \tilde{K}^{(n-1)}(t') \right] e^{i\tilde{M}^{(0)}(t-t')/\hbar}. \qquad \text{(A.9)}$$

The perturbing term $\tilde{M}^{(1)}$ is the transformed form of expression (A.6) and is of course much more involved then the original one. The calculation in this general form is very cumbersome and the explicit expression for $\tilde{\chi}^{(1)}$ is reported in detail in reference [29]. The goal of obtaining a time dependent differential equation for the order parameter in this general situation is subjected to severe restrictions [38, 41].

We work near the critical temperature. Let us consider the relatively simple case where the zeroth order pair potential $\bar{\mu}^{(0)}$ can be neglected. This is obviously the case at $T > T_c$ where $\bar{\mu}^{(0)}$ is rigorously zero and $\bar{\mu}(t)$ gives the fluctuations of the pair potential and therefore of the order parameter. The equation obtained is therefore connected to the relaxation of the order parameter towards the equilibrium condition $\Delta \equiv 0$.

At $T < T_c$ we need either that a characteristic frequency ω of the system is much greater than Δ_0 or to be in the gapless regime.

Under the previous hypothesis $\bar{M}^{(1)}$ contains the full self-potential $\bar{\mu}$:

$$\bar{M}^{(1)} = \begin{pmatrix} 0 & \bar{\mu} \\ -\bar{\mu}^* & 0 \end{pmatrix} \qquad \text{(A.10)}$$

and the expression for $\bar{M}^{(0)}$ reduces to the usual kinetic term i.e.

$$\bar{M}^{(0)} = \begin{pmatrix} \epsilon & 0 \\ 0 & -\epsilon \end{pmatrix}.$$

We have therefore

$$e^{i\bar{M}^{(0)}(t-t')/\hbar} = \begin{pmatrix} e^{i\epsilon(t-t')/\hbar} & 0 \\ 0 & e^{-i\epsilon(t-t')/\hbar} \end{pmatrix}.$$

We can now start from eq.(A.8) for $\bar{K}^{(n)}$. At first order we have:

$$\begin{pmatrix} \bar{h}^{(1)} & \bar{\chi}^{(1)} \\ -\bar{\chi}^{*(1)} & 1 - \bar{h}^{*(1)} \end{pmatrix} = -\frac{i}{\hbar}\int_{-\infty}^{t} dt' \begin{pmatrix} e^{-i\epsilon(t-t')/\hbar} & 0 \\ 0 & e^{i\epsilon(t-t')/\hbar} \end{pmatrix}$$

$$\left[\begin{pmatrix} 0 & \bar{\mu} \\ -\bar{\mu}^* & 0 \end{pmatrix}, \begin{pmatrix} \bar{h}^{(0)} & \bar{\chi}^{(0)} \\ -\bar{\chi}^{*(0)} & 1 - \bar{h}^{*(0)} \end{pmatrix}\right] \begin{pmatrix} e^{i\epsilon(t-t')/\hbar} & 0 \\ 0 & e^{-i\epsilon(t-t')/\hbar} \end{pmatrix}. \qquad (A.11)$$

Working with spin independent forces, in the k representation the preceding equation gives rise to

$$\bar{h}^{(1)}_{k,k'} = 0,$$

$$\bar{\chi}^{(1)}_{k,k'}(t) = -\frac{i}{\hbar}\int_{-\infty}^{t} dt' e^{-i(\epsilon_k+\epsilon_{k'})(t-t')/\hbar}\Delta_{k,k'}(t')\left(1 - \bar{h}^{*(0)}_k - \bar{h}^{(0)}_{k'}\right). \qquad (A.12)$$

We have used the approximation (3.23) for the order parameter where

$$\Delta = \int d(\mathbf{x}_1 - \mathbf{x}_2)\bar{\mu}(\mathbf{x}_1, \mathbf{x}_2)$$

in the approximation $\bar{E}_k = |\epsilon_k|$ $(\Delta^{(0)} = 0)$

$$\begin{aligned} \bar{h}^{(0)}_{k,k'} &= \bar{h}_k \delta_{k,k'} \\ \bar{h}_k &= \frac{1}{1+exp(\beta\epsilon_k)} \\ 1 - \bar{h}_k - \bar{h}_{k'} &= \frac{1}{2}\left(th\frac{\beta\epsilon_k}{2} + th\frac{\beta\epsilon_{k'}}{2}\right) \\ &\equiv \frac{1}{2}\left(\theta + \theta'\right). \end{aligned} \qquad (A.13)$$

At the second order for the relevant quantities $\bar{\chi}^{(2)}$ and $\bar{h}^{(2)}$ we have:

$$\bar{\chi}^{(2)} = 0$$

$$\bar{h}^{(2)}(t) = -\frac{i}{\hbar}\int_{-\infty}^{t} dt' e^{-i\epsilon(t-t')/\hbar}\left(-\bar{\mu}(t')\bar{\chi}^{*(1)}(t') + \bar{\chi}^{(1)}(t')\bar{\mu}^*(t')\right)e^{i\epsilon(t-t')/\hbar} \qquad (A.14)$$

and similarly

$$\bar{h}^{(3)} = 0$$

$$\bar{\chi}^{(3)}(t) = -\frac{i}{\hbar} \int_{-\infty}^{t} dt' e^{-i\epsilon(t-t')/\hbar} \left(-\bar{\mu}(t')h^{*(2)}(t') + \bar{h}^{(2)}(t')\bar{\mu}^{*}(t') \right) e^{-i\epsilon(t-t')/\hbar}. \quad \text{(A.15)}$$

In general we have:

$$\bar{h}^{(2n+1)} = 0 \quad \bar{\chi}^{(2n)} = 0. \quad \text{(A.16)}$$

The k representations of eq.(A.14) and (A.15) are easily obtained. Of course they are greatly involved. For instance $\bar{h}_{k,k'}^{(2)}(t)$ is

$$\bar{h}_{k,k'}^{(2)}(t) = \frac{1}{2}(\frac{i}{\hbar})^2 \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt_1 e^{-i(\epsilon_k - \epsilon_{k'})(t-t')/\hbar}$$

$$\sum_{k_1} \{ \Delta_{k,k_1}(t') \Delta_{k_1,k'}^{*}(t')(\theta_1 + \theta') e^{i(\epsilon_{k_1} + \epsilon_{k'})(t'-t_1)/\hbar}$$

$$+ \Delta_{k,k_1}(t') \Delta_{k_1,k'}^{*}(t')(\theta_1 + \theta) e^{-i(\epsilon_{k_1} + \epsilon_k)(t'-t_1)/\hbar} \}. \quad \text{(A.17)}$$

We have taken the matrix elements of equation (A.14) and used eq.(A.12). The expression (A.17) for $\bar{h}^{(2)}$ will be used to calculate the current and the density.

We now proceed to calculate the equation for the order parameter Δ. The self-consistent equation for Δ up to the third order in $\bar{\mu}$ is

$$\Delta(x) = -g \left(\bar{\chi}^{(1)}(x,x) + \bar{\chi}^{(3)}(x,x) \right) \quad \text{(A.18)}$$

where according to the explicit expression (A.12) for $\bar{\chi}_{k,k_1}^{(1)}$ and the matrix form for $\bar{\chi}^{(3)}$, both $\bar{\chi}^{(1)}$ and $\bar{\chi}^{(3)}$ are in turn functions of Δ evaluated at different points in space and time. Here $\Delta(x)$ with $x \equiv (\mathbf{x}, t)$. In the presence of a slowly varying external field $(\mathbf{A}, V)$ we restrict ourselves to the quasi-classical approximation for the single particle wave function $g_k(x)$

$$g_k(x) = e^{i\frac{e}{\hbar}Ax} w_k(x) \quad \text{(A.19)}$$

where we have used the four vector notation $A = (\mathbf{A}, V)$ with $\mathbf{A}$ the vector potential and V the scalar potential. $w_k(x)$ are the single particle wave functions in the absence of external fields and are chosen to be real. We have now

$$\bar{\mu}_{k,k'}(t) \sim \Delta_{k,k'}(t) = \int d\mathbf{x} \Delta(\mathbf{x}, t) g_k^{*}(\mathbf{x}, t) g_{k'}^{*}(\mathbf{x}, t) \quad \text{(A.20)}$$

and

$$\bar{\chi}(x, x) = \sum_{\mathbf{k}, \mathbf{k'}} g_{\mathbf{k}}(x) g_{\mathbf{k'}}(x) \chi_{\mathbf{k}, \mathbf{k'}}(t). \tag{A.21}$$

The self-consistent eq.(A.18) for the order parameter can be written

$$\Delta(x) = \frac{i}{2} \frac{g}{\hbar} \sum_{\mathbf{k}, \mathbf{k'}} \int_{-\infty}^{t} dt' \int dx' exp(-i(\epsilon_{\mathbf{k}} + \epsilon_{\mathbf{k'}})(t - t')/\hbar)$$

$$\Delta(x') g_{\mathbf{k}}^*(x') g_{\mathbf{k'}}^*(x') g_{\mathbf{k}}(x) g_{\mathbf{k'}}(x)(\theta + \theta') + third \ order \ terms \tag{A.22}$$

We have used eq.(A.12),(A.13),(A.20) and (A.21).

Assuming slow variation in space an time (among other things the semiclassical approximation fails otherwise), we expand the exponential (A.19) and $\Delta(x')$ in a Taylor series about the point x according to a standard procedure used in the time independent problem, as for instance in [43] where highly concentrated alloys are discussed and results are given in terms of scattering time only as in the case of the dilute systems [15]. We obtain:

$$\Delta(x') g_{\mathbf{k}}^*(x') g_{\mathbf{k'}}^*(x') g_{\mathbf{k'}}(x) g_{\mathbf{k}}(x) = w_{\mathbf{k}}(x') w_{\mathbf{k'}}(x') w_{\mathbf{k'}}(x) w_{\mathbf{k}}(x)$$

$$\left[\Delta(x) + \sum_{\alpha=1}^{4} (x' - x)_\alpha \bar{\delta}_\alpha \Delta(x) + \frac{1}{2} \sum_{\alpha, \beta=1}^{4} (x' - x)_\alpha (x' - x)_\beta \bar{\delta}_\alpha \bar{\delta}_\beta \Delta(x) \right] \tag{A.23}$$

where

$$\bar{\delta}_\alpha \equiv \partial_\alpha - \frac{2ieA_\alpha}{\hbar}. \tag{A.24}$$

Note the factor two in the derivative due to the pair condensation.

Apart from calculation, it is clear now how to get a differential equation for Δ. We substitute eq.(A.23) into eq.(A.22) and obtain Δ as a function of Δ itself and its derivative; each term contains a coefficient which has to be calculated by integration:

$$\Delta = Q\Delta + \sum_{\alpha=1}^{4} S_\alpha \bar{\delta}_\alpha \Delta +$$

$$+ \frac{1}{2} \sum_{\alpha, \beta=1}^{4} L_{\alpha, \beta} \bar{\delta}_\alpha \bar{\delta}_\beta \Delta + R|\Delta|^2 \Delta. \tag{A.25}$$

The third term has not been discussed explicitly here and is the same as in the time-independent case [43]:

$$R = -gN_0 \frac{7\zeta(3)}{8(\pi K_B T_c)^2}.$$ (A.26)

where N_0 is the density of states at the Fermi energy $N_0 = (mp_F/2\pi^2\hbar^3)$. After integration over time, coefficients Q and $L_{i,j}$ $(i,j = 1,2,3)$ of the term with no time derivative reduce to the usual time-independent values:

$$Q = 1 + gN_0 \frac{T_c - T}{T_c}$$ (A.27)

and in the isotropic case

$$\frac{1}{2}L_{i,j} = N_0 L^2 \delta_{i,j} \qquad L^2 = \begin{array}{ll} \frac{\hbar^2}{2m} \frac{7\zeta(3)E_F}{12(\pi k_B T_c)^2} & for\ clean\ superconductors \\ \frac{\pi}{24} \frac{\hbar v_F^2 \tau}{k_B T_c} & for\ dirty\ superconductors \end{array}$$ (A.28)

τ is the scattering time, v_F and E_F are the Fermi velocity and energy respectively. We do not perform explicitly the calculations because they are widely discussed in the literature. Starting from ref.[29] where they are derived, the reader can also easily make a connection with all the other papers where they are given explicitly [15, 42, 37, 38, 43], especially with ref.[43]. We shall rather discuss fully the time-dependent terms. The mixed terms containing both time and space derivative vanish by symmetry owing to the presence of the factor $\mathbf{x}' - \mathbf{x}$ in $L_{i,j}$ $(i,j = 1,2,3)$. The same applies to coefficients S_i. So that we are left with S_4 and L_{44} only, i.e. the coefficients of the terms containing the first and second time derivative of the order parameter, respectively. The last two terms give the time dependent correction to the ordinary time independent Landau-Ginzburg equation.

We write them explicitly:

$$S_4 = i\frac{g}{2\hbar} \sum_{\mathbf{k},\mathbf{k}'} \int_{-\infty}^{t} dt' exp\left[i\left(\epsilon_{\mathbf{k}} + \epsilon_{\mathbf{k}'} - i\eta\right)(t' - t)/\hbar\right]$$

$$(t' - t)(\theta + \theta') < w_{\mathbf{k}}(\mathbf{x}')w_{\mathbf{k}'}(\mathbf{x}')w_{\mathbf{k}'}(\mathbf{x})w_{\mathbf{k}}(\mathbf{x}) >,$$ (A.29)

$$L_{44} = i\frac{g}{2\hbar} \sum_{\mathbf{k},\mathbf{k}'} \int_{-\infty}^{t} dt' exp\left[i\left(\epsilon_{\mathbf{k}} + \epsilon_{\mathbf{k}'} - i\eta\right)(t' - t)/\hbar\right]$$

$$(t' - t)^2 (\theta + \theta') < w_{\mathbf{k}}(\mathbf{x}')w_{\mathbf{k}'}(\mathbf{x}')w_{\mathbf{k}'}(\mathbf{x})w_{\mathbf{k}}(\mathbf{x}) >, \qquad (A.30)$$

where the η is an adiabatic switching on parameter and the the brackets $< ... >$ denote the averaging procedure over the impurities if they are present. Let us calculate S_4 by way of example. We integrate eq.(A.29) over x' and sum over $\mathbf{k}'$ and get

$$S_4 = i\frac{g}{\hbar}\sum_{\mathbf{k}} \theta < |w_{\mathbf{k}}(\mathbf{x})|^2 > \frac{1}{(2\epsilon_{\mathbf{k}} - i\eta)^2/\hbar^2}. \qquad (A.31)$$

Remembering that around the Fermi energy

$$\sum_{\mathbf{k}\in S_F} < w_{\mathbf{k}}(\mathbf{x})w_{\mathbf{k}}(\mathbf{x}) >= N_0$$

and

$$\theta = th\frac{\epsilon_{\mathbf{k}}}{2T} = 2T\sum_{\omega_n}\frac{1}{\epsilon_{\mathbf{k}} - i\omega_n}$$

with $\omega_n = (2n+1)\pi k_B T$ we can use the countour integration to get

$$S_4 = ig\hbar N_0 \int_{-\infty}^{\infty} d\epsilon\frac{\theta(\epsilon)}{(2\epsilon - i\eta)^2} = -g\frac{N_0\pi\hbar}{8k_B T_c}. \qquad (A.32)$$

Using a similar procedure one obtains

$$L_{4,4} = gN_0\frac{7\zeta(3)}{8(\pi k_B T_c)^2}. \qquad (A.33)$$

With the previous values (A.26,A.27,A.32,A.33) of the coeffcients we get the time-dependent Landau-Ginzburg equation for the order parameter

$$A\Delta + B\left[|\Delta|^2 - \frac{\hbar^2}{2}\left(\frac{\partial}{\partial t} + 2ieV/\hbar\right)^2\right]\Delta - C\left(\nabla - \frac{2ie}{\hbar}\mathbf{A}\right)^2\Delta +$$

$$+ G\left(\frac{\partial}{\partial t} + 2ieV/\hbar\right)\Delta = 0 \qquad (A.34)$$

where

$$A = N_0\frac{T - T_c}{T_c}, \quad B = N_0\frac{7\zeta(3)}{8(\pi k_B T_c)^2}, \quad C = N_0 L^2, \quad G = \frac{N_0\pi\hbar}{8k_B T_c}. \qquad (A.35)$$

Eq.(A.34) is the time dependent Landau Ginzburg equation for the fluctuating order parameter. Within the approximations considered the second time derivative can be

neglected. When Δ is time independent eq.(A.34) reduces to the ordinary Landau-Ginzburg equation but for a normalization factor (3.24)

$$\Delta = \left(\frac{\hbar^2}{2mC}\right)^{1/2}\psi = Z^{-1/2}\psi \qquad (A.36)$$

and we get the explicit expressions for the Landau-Ginzburg parameters

$$a' = Z^{-1}A, \quad b = Z^{-2}B, \quad \gamma = Z^{-1}G \qquad (A.37)$$

reported in eq.(7.52).

The current in terms of the density matrix [33]is

$$\mathbf{J}(\mathbf{x}) = -i\frac{e\hbar}{m}(\nabla_{\mathbf{x}} - \nabla_{\mathbf{x}'})\bar{h}(\mathbf{x},\mathbf{x}',t)|_{\mathbf{x}=\mathbf{x}'} - \frac{2e^2}{m}\mathbf{A}(\mathbf{x})\bar{h}(\mathbf{x},\mathbf{x},t). \qquad (A.38)$$

In the k representation this becomes

$$\mathbf{J}(x) = -(ie\hbar/m)\sum_{\mathbf{k},\mathbf{k}'}\bar{h}_{\mathbf{k},\mathbf{k}'}(t)\,(g_{\mathbf{k}'}^*\nabla g_{\mathbf{k}} - g_{\mathbf{k}}\nabla g_{\mathbf{k}'}^*) - (2e^2/m)A(x)\bar{h}(x,x). \qquad (A.39)$$

Whithin the semi-classical approximation (A.19) the current is given by

$$\mathbf{J}(x) = -(ie\hbar/m)\sum_{\mathbf{k},\mathbf{k}'}\bar{h}_{\mathbf{k},\mathbf{k}'}(t)\,(w_{\mathbf{k}'}\nabla w_{\mathbf{k}} - w_{\mathbf{k}}\nabla w_{\mathbf{k}'}). \qquad (A.40)$$

Since $\bar{h}_{\mathbf{k},\mathbf{k}'}^{(0)}$ is diagonal, $\bar{h}_{\mathbf{k},\mathbf{k}'}^{(1)}$ is identically zero and $\bar{h}_{\mathbf{k},\mathbf{k}'}^{(2)}$ vanishes when $\Delta = 0$, we do not have the ohmic current. This is due to approximation (A.19) which is valid for a nearly constant V. Using expression (A.17) for $\bar{h}_{\mathbf{k},\mathbf{k}'}^{(2)}$ where the Δ's are transformed in configuration space by means of the $g_{\mathbf{k}}$'s we can again expand Δ and $g_{\mathbf{k}}$ as in the equation for Δ itself. The contribution to the current of the time derivative of Δ vanishes and $\mathbf{J}$ reduces to the time independent [43] expression

$$\mathbf{J}(x) = 2ie\hbar N_0 L^2\left[\Delta\left(\nabla + \frac{2ie}{\hbar}\mathbf{A}\right)\Delta^* - \Delta^*\left(\nabla - \frac{2ie}{\hbar}\mathbf{A}\right)\Delta\right]. \qquad (A.41)$$

where L^2 is given by eq.(A.28). With the normalization factor (A.36) $\mathbf{J}$ is identical to the phenomenological expression (4.8).

The charge density fluctuation is given in the k representation by

$$\bar{h}^{(2)}(x) = 2e\sum_{\mathbf{k},\mathbf{k}'}\bar{h}_{\mathbf{k},\mathbf{k}'}^{(2)}(t)g_{\mathbf{k}'}^*(x)g_{\mathbf{k}}(x). \qquad (A.42)$$

By taking now the time derivative of this last equation and performing the calculations according the lines previously discussed, we obtain the following expression

$$\frac{\partial \bar{h}^{(2)}(t)}{\partial t} = -2div\mathbf{J} - 2ie \left(\frac{\hbar^2 B}{2} \frac{\partial}{\partial t} - G \right) \left(\Delta \left(\frac{\partial}{\partial t} - 2ieV/\hbar \right) \Delta^* - c.c \right). \quad (A.43)$$

If we now use the time dependent Landau-Ginzburg equation for the order parameter, we can show that a continuity equation holds

$$\frac{\partial h^{(2)}(t)}{\partial t} + div\mathbf{J} = 0. \quad (A.44)$$

Hence, within the approximations used, the charge is conserved if and only if the equation of motion for the order parameter is satisfied .

Further we note that by putting $\Delta = |\Delta|e^{i\theta}$, the equation for the density becomes

$$\frac{\partial h^{(2)}(t)}{\partial t} = 4e \left(\frac{\hbar^2 B}{2} \frac{\partial}{\partial t} - G \right) \left(\left(\dot{\theta} + 2eV/\hbar \right) |\Delta|^2 \right), \quad (A.45)$$

which implies that the density is constant and the system is stationary whenever the Josephson eq.(4.14) is satisfied.

We have so established a close connection between the microscopic theory and the phenomenological approach discussed in the first four lectures and derived the second from the first one. Besides the other restrictions previously discussed, the validity of equation (A.34) for Δ is restricted to the validity of the mean field approximation, i.e. the present theory is included in the class of the so called "classical" theories plus corrections due to small fluctuations. Hence any result we derive from eq.(A.34) will fail too close to the critical point where corrections due to the scaling theory of critical phenomena have to be added.

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