Lecture Notes

QUANTUM STATISTICAL FIELD THEORY

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Chapter 1

QUANTUM STATISTICAL MECHANICS

The problem to explain macroscopic phenomena in terms of the properties of the microscopic constituents of matter is basically a quantum-mechanical one. Not only is quantum mechanics, rather than classical mechanics, believed to be the correct description at the atomic and subatomic scale, but also many macroscopic phenomena are evidently of a quantum nature. For example, superconductivity and superfluidity are of quantum origin, while more generally the third law of thermodynamics is a quantum law.

At the microscopic level the properties of a many-particle system are described by the wave function and the Schrödinger equation that determines the behaviour of the assembly in time. However, in view of the huge number ($\sim 10^{24}$) of particles, the detailed specification of the initial state and the solution of this equation would too complex to even be contemplated. Even if one could solve the problem with the aid of a supercomputer, the solution would be so complicated as to be completely unintelligible. What is needed foremost is a precise characterization of a set of state variables relevant to macroscopic systems.

In the following we will often use some notations borrowed from relativity theory. A space-time point will be indicated as $x = x^\mu = (t, \mathbf{x}), \mu = 0, 1, 2, 3$, and particle energy-momentum as $p = p^\mu = (p_0, \mathbf{p})$. Gradient and time derivative are sometimes combined: $\partial\mu = (\partial_t, \nabla), \partial^\mu = (\partial_t, -\nabla)$. Furthermore, we will often write $x.p = x_\mu p^\mu = x^\mu p_\mu$ for $tp_0 - \mathbf{x}.\mathbf{p}$, and use the Einstein convention. Natural units $\hbar = c = k_B = 1$ are adopted throughout.

1.1 Observables and States

We start by introducing two concepts for describing an arbitrary system in the most basic terms, namely those of observable and state [1].

An observable represents a quantity which may, in principle, be measured. In quantum mechanics there is a one-to-one correspondence between the observables A of a system, and the self-adjoint operators $\hat{A}$ acting on a Hilbert space $\mathcal{H}$. In an axiomatic context the quantum mechanical system is specified by giving an algebra of operators $\mathcal{A}$ whose observables (i.e. the self adjoint elements) correspond to the given physical system.

A state, on the another hand, is a statistical quantity which serves to determine the expectation values $\rho(A)$ of the observables, should any of them be measured. Hence we may describe states, in a general manner, as functionals of the observables, which yield their expectation values under specified experimental conditions. These conditions are controlled by external parameters which may correspond to system volume, gravitational field, temperature, density, etc. Now in standard quantum mechanics of finite systems, i.e. systems confined to a volume V, pure states are represented by normalized vectors $|\psi >$ in a Hilbert space $\mathcal{H}$. The expectation value in this state is defined as

$$\rho_\psi (A) =< \psi|\hat{A}|\psi > . \tag{1.1}$$

The quantum mechanical description of a physical system is therefore defined by the Hilbert-space representation of its states and observables. For a many-particle system it is beyond experiment to determine any unique micro-state of the system. The available information is usually compatible with very many micro-states $|\psi_k >, k = 1, 2, \ldots,$ with respective probabilities p_k. The expectation value of an observable is then defined as

$$\rho (A) = \sum_k p_k \rho_k(A) = \sum_k p_k < \psi_k|\hat{A}|\psi_k > . \tag{1.2}$$

Inserting a complete set of states we get

$$\rho(A) = \mathrm{Tr}\hat{\rho}\hat{A}, \tag{1.3}$$

where the trace may be taken with respect to any arbitrary complete set of states. The density operator defined by

$$\hat{\rho} = \sum_k |\psi_k > p_k < \psi_k| \tag{1.4}$$

corresponds to a statistical mixture of pure states which is generally termed a mixed state, or an ensemble of states. It important to note that the set $|\psi_k >$ need not to be defined in terms orthonormal states. Any state can be represented in the form (1.4), and it follows that the correspondence between ρ and $\hat{\rho}$ is one-to-one. Note that (1.3) has the form of an inner product; hence states and observables can be pictured as belonging to dual vector spaces.

Exercise 1.1

a. Using $p_k \geq 0$ and $\Sigma p_k = 1$, show that $\hat{\rho}$ is a density operator, i.e. a positive operator of unit trace.

b. Show that a pure state is characterized by $\hat{\rho}$ being idem-potent, i.e. $\hat{\rho}^2 = \hat{\rho}$.

c. Verify that $\mathrm{Tr}\hat{\rho}^2 < 1$ for a mixed state.

It is important to note that $\hat{\rho}$ contains two different aspects of probability: that inherent in quantum mechanics itself, as well as that associated with incomplete information regarding the state of the system. In most cases it is extremely difficult to distinguish between the two. Indeed even for a microscopic system the infinite extent of the relevant Hilbert space usually renders complete specification of $\hat{\rho}$ impossible.

In the Schrödinger picture the state of the system evolves according to a one-parameter group of unitary transformations

$$\hat{\rho}_t = e^{-i\hat{H}t}\hat{\rho}e^{i\hat{H}t}, \tag{1.5}$$

and the time dependence of the expectation value of an observable is therefore

$$\rho_t(A) = \mathrm{Tr}\hat{\rho}_t\hat{A}. \tag{1.6}$$

The self-adjoint generator $\hat{H}$ of the transformation $\rho \to \rho_t$ is termed the Hamiltonian of the system. In principle, it is a state-dependent quantity, its form being governed by the state ρ as well as the interactions in the system. For conservative systems, $\hat{H}$ represents the energy variable.

One can equally well describe the dynamics in the Heisenberg picture where the evolution of the system corresponds to a unitary transformation of the observables:

$$\hat{A}_t = e^{i\hat{H}t}\hat{A}e^{-i\hat{H}t}. \tag{1.7}$$

It follows that $\hat{A}_t$ satisfies the Heisenberg equation of motion

$$\partial_t\hat{A}_t = i[\hat{H}, \hat{A}_t]. \tag{1.8}$$

The identity

$$\rho_t(A) = \rho(A_t) \tag{1.9}$$

expresses the equivalence of the two pictures.

Exercise 1.2

Derive (1.9) and determine the time dependence of $\mathrm{Tr}\hat{\rho}_{-t}\hat{A}_t$.

1.2 Equilibrium

When the available information about the system is very incomplete, one must make optimum use of whatever information can be obtained. In any case, the probability distribution $\{p_k\}$ characterizing the density operator (1.4) must be such that the expectation values of the relevant observables agree with the actually measured values. A system in equilibrium is characterized by its extensive conserved quantities comprising the energy

$$E = \rho(H) \tag{1.10}$$

and a finite number of charges

$$N_a = \rho(Q_a), \tag{1.11}$$

$a = 1, 2, \ldots$. In thermodynamics it is assumed that these conserved quantities form a complete macroscopic description of the equilibrium state in the following sense: given the values (E, N_a) there is precisely one equilibrium state ρ_{eq}. This state is the one that maximizes the entropy of the system. In quantum statistical mechanics the entropy is defined as the following functional of the state:

$$S[\rho] = -\text{Tr}\hat{\rho}\ \log\ \hat{\rho}. \tag{1.12}$$

This is just the quantum-mechanical version of the original definition put forward by Gibbs.

Exercise 1.3

a. Argue that the entropy can be written as

$$S[\rho] = -\sum_n w_n\ \log\ w_n, \tag{1.13}$$

where $\{w_n\}$ are the eigenvalues of $\hat{\rho}$. (Positive Hermitian operators of finite trace can be diagonalized and have purely discrete spectra.)

b. Show that, without constraints, S is maximal for a distribution of equal probabilities, and minimal for any pure state.

The maximum entropy principle allows the determination of a unique density operator $\hat{\rho}_{\text{eq}}$ compatible with the available experimental information given by (1.10) and (1.11). It is the solution of the variational equation

$$\delta S = 0 \tag{1.14}$$

subject to the constraints

$$\text{Tr}\delta\hat{\rho} = 0\ ,\ \ \text{Tr}\delta\hat{\rho}\,\hat{Q}_a = 0,\ \ \text{Tr}\delta\hat{\rho}\hat{H} = 0. \tag{1.15}$$

The variational problem is easily solved with the help of the Lagrange-multiplier method. The result is that $\hat{\rho}_{\text{eq}}$ is equal to the (grand) canonical density operator

$$\hat{\rho}_{\text{c}} = \exp\left(\Phi - \alpha_a\hat{Q}_a - \beta\hat{H}\right) \tag{1.16}$$

with the Lagrange multipliers (Φ, α_a, β) corresponding to the constraints imposed. In particular, the normalization yields the thermodynamic potential

$$\Phi\left(\alpha_a, \beta, V\right) = -\log\ \text{Tr}\exp\left(-\alpha_a\hat{Q}_a - \beta\hat{H}\right) = -\log\ Z, \tag{1.17}$$

in terms of the partition function Z. For the entropy of the equilibrium state we get

$$S[\rho_{\rm c}] = \alpha_a N_a + \beta E - \Phi \tag{1.18}$$

on account of (1.10)–(1.12), and (1.16). We mention that one often characterizes the system in terms of the grand potential Ω which is related to the thermodynamic potential Φ by $\Phi = \beta\Omega$.

We note that the above reasoning is quite general, and can easily be extended to the case that the information about the system is given in the form of expectation values of any number of hermitian operators. Possible non-commutativity of the operators presents no difficulty in carrying out the variational procedure, and the method of Lagrange multipliers leads to a statistical density operator of the canonical form. This is the Gibbs algorithm for constructing a statistical operator when the available information is only macroscopic and much less than complete. The canonical operator does not so much represent the actual state of the system as the most likely state consistent with observations. In fact the maximum entropy principle is nothing but the postulate of equal *a priori* probabilities applied to the case when information is available regarding the expectation values of a number of operators which are constants of the motion [2]; see also 1.2.

We still have to show that the equilibrium state corresponds to a maximum. Instead we will now demonstrate that the canonical state of a finite system is uniquely determined by the thermodynamic stability condition that it minimizes the functional

$$\Phi[\rho] = {\rm Tr}\hat\rho\Big(\log\,\hat\rho + \alpha_a\hat Q_a + \beta\hat H\Big)\,. \tag{1.19}$$

By eqs. (1.16) and (1.19)

$$\Phi(\alpha_a, \beta, V) = {\rm Tr}\hat\rho\Big(\log\,\hat\rho_{\rm c} + \alpha_a\hat Q_a + \beta\hat H\Big) \tag{1.20}$$

from which it follows that

$$\Phi[\rho] - \Phi(\alpha_a, \beta, V) = {\rm Tr}\hat\rho\,\log\,\hat\rho/\hat\rho_{\rm c} \geq 0 \tag{1.21}$$

which is the Gibbs inequality.

Exercise 1.4

> Use the fact that $x\,\log\,x \geq x - 1$ is a strictly convex function of the positive real variable x to derive the Gibbs inequality. See ref [1].

1.3 Thermodynamics

Let us now consider the variations

$$\delta\Phi = N_a\delta\alpha_a + E\delta\beta + \frac{\partial\Phi}{\partial V}\delta V, \tag{1.22}$$

$$\delta S = \alpha_a \delta N_a + \beta \delta E - \frac{\partial \Phi}{\partial V} \delta V, \tag{1.23}$$

implied by (1.17) and (1.18). By identifying the last equation with the Gibbs relation of classical thermodynamics, we can attach the following thermodynamic meaning to the Lagrange multipliers:

$$\alpha_a = -\beta \mu_a, \tag{1.24}$$

$$\beta = T^{-1}, \tag{1.25}$$

$$\beta P = -\frac{\partial \Phi}{\partial V} = -\frac{\Phi}{V}. \tag{1.26}$$

Here P is the pressure, T the temperature, and μ_a the chemical potential associated with the charge $\hat{Q}_a$. We have taken it for granted that Φ is extensive (up to a surface effect) like S, E, N_a. This can in fact be established for finite assemblies of particles with realistic interactions, that is, interactions which are repulsive at short distances and fall off fast enough at large distances to ensure that the energy is an extensive variable.

Exercise 1.5

a. Write equation (1.18), which in thermodynamics is known as the Euler relation, and the Gibbs relation (1.23) in terms of the intensive densities $n_a = N_a/V, e = E/V, s = S/V$.

b. Derive the Gibbs-Duhem relation:

$$\delta P = n_a \delta \mu_a + s \delta T. \tag{1.27}$$

The above formulae show that the conserved global densities and the Lagrange multipliers are two sets of conjugate variables. Indeed, writing $A_i = (N_a, E)$ and $\alpha_i = (\alpha_a, \beta)$, we have

$$\frac{\partial \Phi}{\partial \alpha_i} = A_i, \quad \frac{\partial S}{\partial A_i} = \alpha_i. \tag{1.28}$$

This implies that the thermodynamic potential Φ is a Massieu function, i.e. a Legendre transform of the entropy; see equation (1.18).

The existence of the partition function Z, and hence the absolute convergence of the trace in (1.17), implies that Z is an analytic function of the Lagrange multipliers. Indeed, if $Z(\boldsymbol{\alpha})$ exists for a range of real values $\boldsymbol{\alpha} = \{\alpha_i\}$ of the Lagrange multipliers, then the partition function also exists for a corresponding range of complex values on account of

$$|Z(\boldsymbol{\alpha} + i\boldsymbol{\gamma})| \leq Z(\boldsymbol{\alpha}). \tag{1.29}$$

Since the partition function, being a sum of positive terms, cannot have zeros for real values $\boldsymbol{\alpha}$, the thermodynamic potential Φ is an analytic function near the real axis for finite volume systems.

It is also easy to show that the thermodynamic potential is a concave function. Let us look at the response of the thermodynamic densities due to a change of the Lagrange multipliers. The static susceptibility matrix χ_{ij} which measures this response, is defined by

$$\beta^{-1}\chi_{ij} = -\frac{\partial A_i}{\partial \alpha_j} = -\frac{\partial^2 \Phi}{\partial \alpha_i \partial \alpha_j}. \tag{1.30}$$

Thermodynamic stability requires this matrix to be positive

$$\lambda_i^* \chi_{ij} \lambda_j \geq 0, \tag{1.31}$$

for arbitrary λ_i. This follows immediately when we compute the static susceptibility from statistical mechanics, i.e. formula (1.17). Taking derivatives with respect to the Lagrange multipliers we get

$$\chi_{ij} = \beta \mathrm{Tr} \hat{\rho}_c \delta \hat{A}_i \delta \hat{A}_j, \tag{1.32}$$

where $\delta \hat{A}_i = \hat{A}_i - \mathrm{Tr}\hat{\rho}_c \hat{A}_i$ is the so-called fluctuation of $\hat{A}_i = (\hat{Q}_a, \hat{H})$. (To avoid complications due to non-commutivity of the operators, we have assumed here that $\hat{Q}_a, \hat{H}$ are mutually commuting.) We conclude that the second derivative of the thermodynamic potential with respect to any parameter is always negative. This means that the thermodynamic potential is a concave function of these parameters:

$$\Phi\left(\lambda \alpha_i + (1-\lambda)\, \alpha_i'\right) \geq \lambda \Phi\left(\alpha_i\right) + (1-\lambda)\, \Phi\left(\alpha_i'\right) \tag{1.33}$$

for all allowed values α_i, α_i' and $0 < \lambda < 1$. As a consequence, Φ cannot support a discontinuity in the interior of the range of its arguments. However, it can have a discontinuous derivative. This implies that the necessary and sufficient condition for the uniqueness of the equilibrium state is the differentiability of the thermodynamic potential [1].

Now, the non-differentiability of the thermodynamic potential with respect to some of the parameters, and the existence of two or more equilibrium states, is the distinctive feature of a phase transition. The above reasoning implies that phase transitions in a finite volume system are not possible. On the other hand, since the limit of a sequence of analytic functions is not necessarily analytic, the thermodynamic potentials of an infinite system might have singularities as a manifestation of phase transitions. This may happen if the complex zeros of the partition function pinch the real parameter axis in the infinite-volume limit. In discussing phase transitions it is important, therefore, to introduce the notion of the thermodynamic limit.

We encounter here a fundamental problem of statistical mechanics, namely that the canonical ensemble as defined for a finite system, cannot describe phases of matter that are quantitatively different. For example, ferromagnetic systems have a spontaneous magnetization below the Curie temperature. When spontaneous magnetization is present, the Hamiltonian of the system is invariant under a transformation that changes the sign of the magnetization. However the state of the system is not invariant. When this happens one says that the symmetry is spontaneously broken. This is a situation which typifies a class of phase transitions.

Spontaneous symmetry breaking seems in conflict with the principles of statistical mechanics. Indeed, if the Hamiltonian is invariant under some symmetry transformation

$$\hat{G}\hat{H}\hat{G}^{-1} = \hat{H} \tag{1.34}$$

the canonical state necessarily exhibits the same symmetry

$$\hat{G}\hat{\rho}_{\rm c}\hat{G}^{-1} = \hat{\rho}_{\rm c}. \tag{1.35}$$

(It is assumed that charges are not affected by symmetry transformations). For an infinite system this need not to be true, since $\hat{\rho}_{\rm c}$ has only formal meaning in this limit. Again it seems that the infinite volume limit provides a framework for describing phase transitions characterized not only by singularities in the thermodynamic functions, but also by changes in macroscopic structure, e.g. of symmetry.

These questions will be discussed in more detail later on. First we shall provide some technical background on operator algebras and field theory that will be needed in the sequel.

Chapter 2

OPERATOR ALGEBRA

Having considered quantum statistical mechanics (QSM) of a finite system in terms of the standard Hilbert space description and canonical ensemble, we shall now set up a formalism that can be generalized to infinite systems and field theory. The idealization of the system as an infinite assembly of particles, whose density is finite, exposes in sharp relief certain intrinsic properties of matter that would otherwise be masked by finite size-effects. It is only by passing to the infinite volume limit that one can characterize phase transitions by singularities in the thermodynamic potentials. The formalism also admits theories of phase transitions, characterized not only by thermodynamic singularities, but also by symmetry breakdown corresponding to a certain "macroscopic degeneracy". This will be essential for an understanding of the phenomena of superconductivity and superfluidity.

2.1 Algebraic description

First it is noted that by basing QSM on bounded operators, we can introduce an algebraic structure [1]. We recall that an operator is termed bounded if its norm

$$||\hat{A}|| = \sup||\hat{A}f|| \tag{2.1}$$

exists, as f runs through the normalized vectors of $\mathcal{H}$. Furthermore, we note that since bounded operators are defined on all vectors of $\mathcal{H}$, it follows that the set $\mathcal{U}$ of these operators has an algebraic structure: if λ is a complex number and $\hat{A}, \hat{B}$ belong to $\mathcal{U}$, then $\lambda\hat{A}, \hat{A}+\hat{B}, \hat{A}\hat{B}$, and $\hat{A}^\dagger$ all belong to $\mathcal{U}$. In view of these properties $\mathcal{U}$ is called a *-algebra (star algebra), the star referring to the fact that $\mathcal{U}$ is closed with respect to Hermitian conjugation.

In physics one often has to deal with unbounded operators, e.g. $\hat{H}$. However, one can always express unbounded operators as strong limits $\hat{A} = \lim \hat{A}_N$, $N \to \infty$, of bounded ones. Hence, we may confine ourselves to bounded observables, without loss of physical content because real measurements yield of course finite results.

We further specify the algebra by introducing the notion of a local operator. We will assume that all relevant observables pertinent to a system enclosed in a bounded open spatial region V are given as space integrals of bounded local ones:

$$\hat{A} = \int_V d^3x \; \hat{a}\left(\mathbf{x}\right). \tag{2.2}$$

It follows that if $V \subset V'$, then $\mathcal{U}(V) \subset \mathcal{U}(V')$. The algebra is said to be isotonic with respect to V.

We require local commutativity which means that if V and V' are disjoint the elements of $\mathcal{U}(V)$ commute with those of $\mathcal{U}(V')$. This ensures that observables in disjoint regions can be measured simultaneously.

The algebra will be equipped with a group of automorphisms (i.e. transformations that preserve the algebraic structure) which represent space translations

$$\hat{a}\left(\mathbf{x}\right) = e^{-i\hat{\mathbf{P}}.\mathbf{x}} \hat{a} e^{i\hat{\mathbf{P}}.\mathbf{x}}, \tag{2.3}$$

or infinitesimally

$$\delta_j \hat{a}\left(\mathbf{x}\right) = -i\left[\hat{P}_j, \hat{a}\left(\mathbf{x}\right)\right]. \tag{2.4}$$

The generator $\hat{\mathbf{P}}$ is called the total momentum. For a finite system $\hat{\mathbf{P}}$ is not necessarily conserved, i.e. it does not necessarily commute with $\hat{H}$. By imposing appropriate boundary conditions on the states, e.g. a box with periodic boundary condition, matrix elements of the commutator can be made to vanish (see section 2.4). We formulate this as a property of the algebra; the interaction between the particles is described by a Hamiltonian which is translationally invariant:

$$\delta_j \hat{H} = -i[\hat{P}_j, \hat{H}] = 0 \tag{2.5}$$

The Hamiltonian generates the time translate of a local operator according to

$$\hat{a}\left(t, \mathbf{x}\right) = e^{i\hat{H}t} \hat{a}\left(\mathbf{x}\right) e^{-i\hat{H}t}, \tag{2.6}$$

or

$$\delta_0 \hat{a}(x) = i[\hat{H}, \hat{a}(x)]. \tag{2.7}$$

Exercise 2.1

Show that the dynamics and space translations can formally be represented by the 'covariant' Heisenberg equation of motion

$$i\partial_\mu \hat{a}(x) = [\hat{a}(x), \hat{P}_\mu], \tag{2.8}$$

where $\partial_\mu = (\partial_t, \nabla), x = (t, \mathbf{x}) \quad \text{and} \quad \hat{P}_\mu = (\hat{H}, -\hat{\mathbf{P}})$.

The structure of the operator algebra as described above applies to bounded local operators for arbitrary regions V. This structure is now carried over to the infinite system by forming the union U of all local algebras [1].

Since states assign numbers to observables, the states of the infinite system are assumed to be functionals of the local observables $\hat{a}$ for which the limit

$$\rho\,(a) = \lim_{V\to\infty} (\mathrm{Tr}\hat{\rho}\hat{a})_V \tag{2.9}$$

$\hat{a} \in \mathcal{U}(V)$, exists. It follows that these states, like those of the finite system, possess the properties of linearity, normalization, and positivity, that is,

$$\rho(\lambda a + \mu b) = \lambda\rho(a) + \mu\rho(b), \tag{2.10}$$

$$\rho(I) = 1, \tag{2.11}$$

$$\rho(a^\dagger a) \geq 0. \tag{2.12}$$

In other words, states preserve addition, scale, and positivity.

Equilibrium states, in particular, are characterized by the Kubo-Martin-Schwinger, or KMS, condition

$$\rho(a_t b) = \rho(b a_{t+i\beta}). \tag{2.13}$$

which plays an important role in axiomatic QSM. The form (2.13) is valid if the conserved charges commute with both a and b.

Exercise 2.2

a. Use the cyclical property of the trace to show that the canonical density operator (1.16) satisfies the KMS condition.

b. Then try to show that the converse is also true [1].

Within the context of the algebraic description the KMS condition is carried over to the infinite system as a key property of its equilibrium states. The KMS condition may then be precisely stated in the following form: for each pair of local observables a, b there is a function $f(z)$ that is analytic in the strip $0 < \mathrm{Im}\, z < \beta$ and continuous on its boundaries such that

$$f(t) = \rho(b a_t), \tag{2.14}$$

$$f(t + i\beta) = \rho(a_t b), \tag{2.15}$$

for real t. The advantage of this formulation is that we avoid reference to complex-time translates, which are not always definable for infinite systems.

2.2 Local Conservation Laws

Conservation laws in physics are attributed to symmetry principles. The invariance of the physical system under certain symmetry transformations implies an appropriate set of conservation laws. Familiar examples are: time translation invariance $\leftrightarrow$ energy conservation, and spatial translation invariance $\leftrightarrow$ momentum conservation.

In quantum mechanics a conservation law is equivalent to the statement that the corresponding operator commutes with $\hat{H}$. For example, conservation of particle number means that the number operator $\hat{N}$ commutes with $\hat{H}$: $\delta_0 \hat{N} = i[\hat{H}, \hat{N}] = 0$. The corresponding symmetry is called rigid gauge invariance, i.e. the invariance of all observables under the transformation

$$\hat{a}_\lambda = e^{-i\lambda\hat{N}} \hat{a} e^{i\lambda\hat{N}} \tag{2.16}$$

with λ a constant. The fact that observables are gauge invariant means that they all commute with $\hat{N}$. This leads to a superselection rule. Namely, the Hilbert space splits up into different sectors each labelled by different eigenvalues of $\hat{N}$. Physical states lie entirely in these sectors, that is, the superposition principle of ordinary quantum mechanics does not apply to vectors belonging to different sectors. Such superselection rules always occur whenever an operator exists that commutes with all observables. Another example is the superselection rule forbidding the superposition of bosonic and fermionic states. In the abstract algebraic approach adopted in this chapter superselection rules can be incorporated in a most natural manner [2].

Let us now assume that the global generators can be written as local integrals:

$$\hat{N} = \int d^3x \; \hat{j}^0(\mathbf{x}) \tag{2.17}$$

$$\hat{H} = \int d^3x \; \hat{t}^{00}(\mathbf{x}) \tag{2.18}$$

$$\hat{P}^i = \int d^3 \; x \hat{t}^{0i}(\mathbf{x}), \tag{2.19}$$

where the integrands are the particle density $\hat{n}(\mathbf{x}) = \hat{j}^0(\mathbf{x})$, the energy density $\hat{e}(\mathbf{x}) = \hat{t}^{00}(\mathbf{x})$, and the momentum density $\hat{t}^{0i}(\mathbf{x}) = \hat{t}^{i0}(\mathbf{x})$, respectively. To ensure that the global quantities are indeed constants of the motion, we require that the local densities satisfy the local conservation laws

$$\partial_\mu \hat{j}^\mu(x) = 0, \tag{2.20}$$

$$\partial_\mu \hat{t}^{\mu\nu}(x) = 0, \tag{2.21}$$

where $\hat{j}^i$ is the particle current density, and $\hat{t}^{ij} = \hat{t}^{ji}$ the microscopic pressure tensor. The time derivative of the generators (2.17) through (2.19) then equals a surface integral which can be made to vanish by imposing suitable boundary conditions; see the next section below.

We note in passing that the formal expressions (2.17)–(2.19) for the global generators are undefined in the thermodynamic limit. However, commutators with these quantities usually exist provided that we commute first and then perform the integration.

The local conservation laws and the known effect of the generators on local observables can be used to put some constraints on equal time commutators between the local densities. Two examples are considered in exc.2.3.

Exercise 2.3

Check that the commutator functions

$$[\hat{j}^0(\mathbf{x}), \hat{j}^0(\mathbf{x}')] = 0, \tag{2.22}$$

$$i[\hat{j}^0(\mathbf{x}), \hat{t}^{00}(\mathbf{x}')] = \hat{\mathbf{j}}(\mathbf{x}').\nabla\delta(\mathbf{x}-\mathbf{x}'), \tag{2.23}$$

are compatible with the conservation laws, and the fact that $\hat{N}$ and $\hat{H}$ are the generators of gauge transformations and time translations, respectively.

However, such equal-time commutation relations are not unique, because one can always add terms involving higher derivatives of the δ-function which vanish upon spatial integration. Terms of this type are called Schwinger terms. Their occurrence cannot always be avoided; this depends on the model under consideration.

Other commutators may be constructed by a similar reasoning. For example, the naive expression for the current/momentum density commutator consistent with locality and conservation laws is

$$i[\hat{j}^0(\mathbf{x}), \hat{t}^{0i}(\mathbf{x}')] = -\hat{j}^0(\mathbf{x}')\partial^i\delta(\mathbf{x}-\mathbf{x}'), \tag{2.24}$$

where $\partial^i = -\nabla_i$. In the non-relativistic theory the momentum density is equal to the mass current: $t^{0i} = mj^i$. Therefore, we may also conclude

$$i\left[\hat{n}\left(\mathbf{x}\right), \hat{\mathbf{j}}\left(\mathbf{x}'\right)\right] = \frac{1}{m}\hat{n}\left(\mathbf{x}'\right)\nabla\delta\left(\mathbf{x}-\mathbf{x}'\right). \tag{2.25}$$

One further example is

$$i\left[\hat{t}^{00}\left(\mathbf{x}\right), \hat{t}^{00}\left(\mathbf{x}'\right)\right] = \left[\hat{t}^{0j}\left(\mathbf{x}\right) + \hat{t}^{0j}\left(\mathbf{x}'\right)\right]\nabla_j\delta\left(\mathbf{x}-\mathbf{x}'\right). \tag{2.26}$$

For the full list of equal-time commutator expressions that can be derived in this manner we refer to the literature [3].

2.3 Field Theory

We now describe an explicit construction of the local algebra in accordance with the above requirements. The experience with the quantization of point-mechanical systems suggests that we should look for a description of the theory in terms of conjugate pairs of variables whose equal-time commutator rules we expect to be of the form

$$[\hat{\phi}(\mathbf{x}), \hat{\pi}(\mathbf{x}')] = i\delta(\mathbf{x}-\mathbf{x}') \tag{2.27}$$

with the commutators $[\hat{\phi}, \hat{\phi}]$ and $[\hat{\pi}, \hat{\pi}]$ vanishing. These relations would be the analogue of the canonical commutation relations for a theory with a continuous infinity of degrees of freedom, that is, a field theory.

Let us now try to express the particle number and total momentum operator in terms of such fields. Trial leads to

$$\hat{N} = -i \int d^3x \; \hat{\pi}(\mathbf{x})\hat{\phi}(\mathbf{x}), \tag{2.28}$$

$$\hat{\mathbf{P}} = \int d^3x \; \hat{\pi}(\mathbf{x})\nabla\hat{\phi}(\mathbf{x}). \tag{2.29}$$

One may check that these two operators commute and that the integrands indeed reproduce the local equal-time commutator (2.24). Hence, the canonical commutator (2.27) can be regarded as a consistency requirement on the formalism. Actually one may verify that if the canonical commutation relations are replaced by anti-canonical commutation relations, the latter would also guarantee the same consistency. The physics decides on the correct choice for the system under consideration, that is, whether the system consists of bosons or fermions.

Exercise 2.4

a. Determine

$$\delta_\lambda\hat{\phi} = i\lambda[\hat{N},\hat{\phi}], \quad \delta_\lambda\hat{\pi} = i\lambda[\hat{N},\hat{\pi}] \tag{2.30}$$

with the help of the identity

$$[A, BC]_- = [A, B]_\pm C - B[C, A]_\pm. \tag{2.31}$$

b. Show that the generator of rigid gauge transformations $\hat{N}$ adds a phase factor to the field operators.

In non-relativistic field theory one describes the observables in terms of a quantized field $\hat{\psi}(\mathbf{x})$, called the Schrödinger field, and its hermitian adjoint which satisfy the canonical commutation or anti-commutation relation

$$[\hat{\psi}(\mathbf{x}), \hat{\psi}^\dagger(\mathbf{x}')]_\pm = \delta(\mathbf{x} - \mathbf{x}') \tag{2.32}$$

according to whether the system consists of fermions or bosons. This immediately identifies $\hat{\pi}(\mathbf{x}) = i\hat{\psi}^\dagger(\mathbf{x})$ as the conjugate momentum. Hence

$$\hat{N} = \int d^3x \; \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x}), \tag{2.33}$$

$$\hat{\mathbf{P}} = -\frac{i}{2}\int d^3x \; \hat{\psi}^\dagger(\mathbf{x})\overleftrightarrow{\nabla}\hat{\psi}(\mathbf{x}). \tag{2.34}$$

The gradient in the last formula corresponds to the replacement $\mathbf{p} \to -i\nabla$, or better $\mathbf{p} \to \overleftrightarrow{\nabla}/2i$, where $\overleftrightarrow{\nabla}$ is the difference of the gradient operator acting to the right and left: $\overleftrightarrow{\nabla} := \overrightarrow{\nabla} - \overleftarrow{\nabla}$. This prescription automatically ensures the hermiticity of the local observables. The above immediately suggests that for the free Hamiltonian we write

$$\hat{H}_0 = \int d^3x \; \hat{\psi}\,(\mathbf{x})\,\varepsilon(\overleftrightarrow{\nabla}/2i)\hat{\psi}\,(\mathbf{x}) \tag{2.35}$$

where $\varepsilon(\mathbf{p}) = \mathbf{p}^2/2m$ is the kinetic energy of a free particle.

Exercise 2.5

Check the commutator

$$[\hat{H}_0, \hat{\psi}(\mathbf{x})] = \varepsilon(-i\nabla)\hat{\psi}(\mathbf{x}) \tag{2.36}$$

for both statistics.

Making use of the result of exc. 2.5, we conclude that the Heisenberg equation for the free field takes the form

$$[i\partial_t - \varepsilon(-i\nabla)]\hat{\psi}(t, \mathbf{x}) = 0. \tag{2.37}$$

This simple equation, together with the (anti-)commutation relations, completely specifies the dynamic behaviour of a system consisting of an arbitrary number of free bosons or fermions.

2.4 Momentum space

Since the system is supposed to be translationally invariant, it is convenient to introduce a decomposition into plane waves characterized by momentum vectors $\mathbf{p}$. We assume the system to be in a large box of volume $V = L^3$, and impose periodic boundary conditions. The allowed discrete values of the momentum $\mathbf{p}$ are then $\mathbf{p} = 2\pi\mathbf{n}/L$, where $\mathbf{n}$ is a vector with discrete components $0, \pm 1, \pm 2, \ldots$. With respect to these discrete states the field operator is expanded as

$$\hat{\psi}\,(\mathbf{x})\,\frac{1}{\sqrt{V}}\sum_{\mathbf{p}} e^{i\mathbf{p}.\mathbf{x}}\hat{a}_{\mathbf{p}}. \tag{2.38}$$

The (anti-)commutation relations (2.32) are fulfilled if we require the momentum operators to satisfy

$$\left[\hat{a}_{\mathbf{p}}, \hat{a}^{\dagger}_{\mathbf{p}'}\right]_{\pm} = \delta_{\mathbf{p}\mathbf{p}'} \tag{2.39}$$

This may be verified with the help of the identity

$$\delta\,(x) = \frac{1}{L}\sum_{n} e^{-i\frac{2\pi n x}{L}} \tag{2.40}$$

valid in the interval $0 < x < L$.

Exercise 2.6

a. Express the observables $\hat{N}, \hat{\mathbf{P}}$, and $\hat{H}_0$ in terms of the momentum operators.

b. Verify explicitly that these operators are mutually commuting.

c. Obtain the solution

$$\hat{a}_{\mathbf{p}}(t) = \hat{a}_{\mathbf{p}}e^{-i\omega t} \tag{2.41}$$

of the free Heisenberg equation. Determine the energy ω.

In the thermodynamic limit the sum over the discrete momenta becomes an integral according to

$$\sum_{\mathbf{p}} \rightarrow \frac{V}{(2\pi)^3} \int d^3p, \tag{2.42}$$

and the Kronecker delta a δ-function according to

$$V\delta\mathbf{p}\mathbf{p}' \rightarrow (2\pi)^3 \delta(\mathbf{p}-\mathbf{p}'). \tag{2.43}$$

If we now define momentum operators $\hat{a}(vecp) = \hat{a}_{\mathbf{p}} \left[V/(2\pi)^3\right]^{\frac{1}{2}}$, we may write the expansion (2.38) of the field operator as a Fourier integral

$$\hat{\psi}(\mathbf{x}) = (2\pi)^{-3/2} \int d^3p \; e^{i\mathbf{p}.\mathbf{x}} \hat{a}(\mathbf{p}) \tag{2.44}$$

in terms of momentum operators satisfying the (anti-)commutation rule

$$[\hat{a}(\mathbf{p}), \hat{a}^\dagger(\mathbf{p}')]_\pm = \delta(\mathbf{p}-\mathbf{p}'). \tag{2.45}$$

Before closing this section we like to make one last remark about the infinite-volume limit implicit in the Fourier representation (2.44). In statistical mechanics it is often essential that this limit is taken last, after all other calculations have been performed. When using the continuous representation for convenience one should be aware that an interchange of limits is involved which may not always be harmless. A case in point is Bose condensation.

2.5 Thermodynamic Wick Theorem

It is illuminating to compute the statistical average

$$< \hat{a}^\dagger(\mathbf{p})\, \hat{a}(\mathbf{p}') >_0 = Z_0^{-1} \mathrm{Tr} \left[e^{\beta\left(\mu\hat{N} - \hat{H}_0\right)} \hat{a}^\dagger(\mathbf{p})\, \hat{a}(\mathbf{p}') \right] \tag{2.46}$$

with respect to the (grand) canonical density operator for a free system. This average, normalized by Z_0, is easily calculated because the cyclic invariance of the trace allows us to write

$$< \hat{a}^\dagger(\mathbf{p})\, \hat{a}(\mathbf{p}') >_0 = < \hat{a}(\mathbf{p}')\, \hat{a}^\dagger(\mathbf{p}, \beta, \mu) >_0, \tag{2.47}$$

where we used the abbreviation

$$\hat{a}^\dagger(\mathbf{p}, \beta, \mu) = e^{\beta\left(\mu\hat{N} - \hat{H}_0\right)} \hat{a}^\dagger(\mathbf{p})\, e^{-\beta\left(\mu\hat{N} - \hat{H}_0\right)}. \tag{2.48}$$

In consequence of the simple commutation rules of $\hat{a}^\dagger(\mathbf{p})$, both with $\hat{N}$ and $\hat{H}_0$

$$[\hat{N}, \hat{a}^\dagger(\mathbf{p})] = \hat{a}^\dagger(\mathbf{p}), \tag{2.49}$$

$$[\hat{H}_0, \hat{a}^\dagger(\mathbf{p})] = \varepsilon(\mathbf{p})\hat{a}^\dagger(\mathbf{p}), \tag{2.50}$$

and the general formula

$$e^A B e^{-A} = B + [A, B]_- + \tfrac{1}{2}\,[A, [A, B]_-]_- + \dots, \tag{2.51}$$

we obtain

$$\hat{a}^\dagger(\mathbf{p}, \beta, \mu) = \hat{a}^\dagger(\mathbf{p}) e^{\beta(\mu-\varepsilon)}. \tag{2.52}$$

We substitute this result back into (2.47) and use the (anti-)commutation rules (2.45). Solving for the desired expectation value we get

$$< \hat{a}^\dagger(\mathbf{p})\hat{a}(\mathbf{p}') >_0 = \delta(\mathbf{p} - \mathbf{p}')n(\varepsilon), \tag{2.53}$$

where $n(\varepsilon)$ is the Fermi-Dirac distribution function in the case of fermions and the Bose-Einstein distribution function in the case of bosons, respectively:

$$n\left(\varepsilon\right) = \frac{1}{\exp\, \beta\left(\varepsilon - \mu\right) \pm 1}. \tag{2.54}$$

Hence, in equilibrium, the expectation value (2.53) is diagonal and can be interpreted as the probability density for finding a particle with energy $\varepsilon(\mathbf{p})$.

Exercise 2.7

a. Argue that the essential piece of information needed to derive (2.53) is contained in the KMS condition

$$< \hat{a}(t, \mathbf{p})\hat{a}^\dagger(\mathbf{p}') >_0 = < \hat{a}^\dagger(\mathbf{p}')\hat{a}(t + i\beta, \mathbf{p}) >_0 e^{-\beta\mu}. \tag{2.55}$$

b. Extend the reasoning to obtain

$$\begin{aligned} &< \hat{a}^\dagger\left(\mathbf{p}_1\right) \dots \hat{a}^\dagger\left(\mathbf{p}_n\right) \hat{a}\left(\mathbf{p}'_n\right) \dots \hat{a}\left(\mathbf{p}'_1\right) >_0 \\ &= \sum_{j=1}^{n} < \hat{a}^\dagger\left(\mathbf{p}_1\right) \hat{a}\left(\mathbf{p}'_j\right) >_0 < \hat{a}^\dagger\left(\mathbf{p}_2\right) \dots \hat{a}^\dagger\left(\mathbf{p}_n\right) \hat{a}\left(\mathbf{p}'_n\right) \dots \\ &\hat{a}\left(\mathbf{p}'_j\right) \dots \hat{a}\left(\mathbf{p}'_1\right) >_0 \end{aligned} \tag{2.56}$$

for bosons. How would this formula read for fermions?

c. Show that on account of the gauge invariance of the canonical ensemble

$$< \hat{a}(\mathbf{p})\hat{a}(\mathbf{p}') >_0 = 0, \tag{2.57}$$

and that the average of an odd number of operators vanishes.

The recursion relation derived above implies that the equilibrium average of products of momentum operators factorizes:

$$\begin{aligned} &< \hat{a}^\dagger(\mathbf{p}_1) \dots \hat{a}^\dagger(\mathbf{p}_n)\hat{a}(\widehat{\mathbf{p}'_n)} \dots \hat{a}(\mathbf{p}'_1) >_0 \\ &= \sum_P \left(\pm 1\right)^P \prod_{j=1}^{n} < \hat{a}^\dagger\left(\mathbf{p}_j\right) \hat{a}\left(\mathbf{p}'_j\right) >_0 . \end{aligned} \tag{2.58}$$

The sum runs over all permutations P of the labels of the primed (or unprimed) variables, and the sign factor is the parity of the permutation in the case of fermions. The permutations preserve the Bose symmetry or Fermi antisymmetry of the left-hand side. The factorization rule, together with (2.53), is known as the thermodynamic Wick theorem. It only holds in the absence of interactions and expresses the fact that states of an ideal system are uncorrelated, except for the correlations induced by the statistics.

Chapter 3

BROKEN SYMMETRY

There is a class of phase transitions which is associated with the spontaneous breaking of a continuous symmetry and the presence of long-range order in the system. In such cases the lowest-energy state does not have the same symmetry as the Hamiltonian of the system. There are different types of symmetry that can be broken at a phase transition. For example, in a ferromagnetic system rotational symmetry is broken because a spontaneous magnetization occurs which defines a unique, but arbitrary, direction in space. Likewise, in the superfluid state gauge symmetry is broken.

In a symmetry breaking transition a new macroscopic parameter, the so-called order parameter appears in the state with the lower symmetry. This parameter measures the loss of symmetry. The order parameter may be a scalar, a vector, a tensor, a complex field or some other quantity. In any case the order parameter is zero in the symmetrical state, and its non-zero values uniquely specify the broken state.

In general, the identification of the order parameter is guided by symmetry considerations and by some physical intuition of the nature of the phase transition. In some cases an order parameter may not exist (e.g. the Kosterlitz-Thouless transition in a 2-dimensional classical spin system), or when an order parameter exists, it is not unique since any power also satisfies the definition. Nevertheless, for the cases treated here, a natural choice in terms of the thermodynamic average of some local operator will present itself almost immediately.

We will adopt Landau's definition that a phase transition is classed as being first-order or second-order according to whether the order parameter is discontinuous or not. The hallmark of a first-order transition is the existence of different phases of the transition point. It follows that any transition carrying an abrupt structural change, like the solid-liquid transitions, must be first order. By contrast, the difference between the phase involved in a continuous transition disappears at the critical point and the symmetry properties of the the phases must be closely related. In a continuous transition the phase at lower temperature usually has the lower symmetry (but this need not to be true always). The fact that second-order phase transitions have a connection with symmetry breaking in the sense that the thermodynamic state of the system below the transition point does not exhibit the full symmetry of the Hamiltonian, was recognized by Landau as early as

1937.

3.1 Ferromagnetic system

As an example of a system with broken symmetry we consider the isotropic Heisenberg ferromagnet. The Hamiltonian of this system is

$$\hat{H} = -\tfrac{1}{2}\sum_{\alpha\neq\beta} J_{\alpha\beta}\hat{\mathbf{S}}^{\alpha}\cdot\hat{\mathbf{S}}^{\beta}. \tag{3.1}$$

It describes a system of interacting spins localized at the sites α, β of a rigid lattice, with exchange interaction $J_{\alpha\beta} > 0$. The spin operators $\hat{\mathbf{S}}^{\alpha}$ at different sites commute and the three spin components at each given site have the usual $SO(3)$ commutation relations:

$$\left[\hat{S}_i^{\alpha}, \hat{S}_j^{\beta}\right] = i\varepsilon_{ijk}\hat{S}_k^{\alpha}\delta_{\alpha\beta}. \tag{3.2}$$

The Hamiltonian is invariant under a rigid rotation of all spins since it only depends on their relative orientation. The generator of these rotations is the total spin operator

$$\hat{\mathbf{S}} = \sum_{\alpha}\hat{\mathbf{S}}^{\alpha} \tag{3.3}$$

on account of the commutation relation

$$\delta_k\hat{S}_i^{\alpha} = -i\left[\hat{S}_k, \hat{S}_i^{\alpha}\right] = \varepsilon_{kij}\hat{S}_j^{\alpha}. \tag{3.4}$$

The corresponding formula for a finite rotation of angle $|\theta|$ around the orientation axis defined by θ is

$$\hat{U}\left(\boldsymbol{\theta}\right)\hat{\mathbf{S}}^{\alpha}U^{\dagger}\left(\boldsymbol{\theta}\right) = R\left(\boldsymbol{\theta}\right)\hat{\mathbf{S}}^{\alpha}, \tag{3.5}$$

where $\hat{U}(\boldsymbol{\theta})$ is the unitary operator

$$\hat{U}\left(\boldsymbol{\theta}\right) = e^{-i\boldsymbol{\theta}\cdot\hat{\mathbf{S}}}. \tag{3.6}$$

Formula (3.5) states that the spin operators transform as vectors under rotations. Indeed the 3×3 orthogonal matrix $R(\boldsymbol{\theta})$ represents an element of the group $SO(3)$ as given by

$$R\left(\boldsymbol{\theta}\right) = e^{i\boldsymbol{\theta}\cdot\mathbf{L}}, \tag{3.7}$$

where

$$\left(\mathbf{L}^i\right)_{jk} = -i\varepsilon_{ijk} \tag{3.8}$$

denotes the $SO(3)$ generators in the vector representation.

Exercise 3.1

a. Check (3.4) by expanding formula (3.5)

b. Demonstrate the rotational invariance of $\hat{H}$ by calculating

$$\delta_k \hat{H} = -i \left[\hat{S}_k, \hat{H}\right] = 0. \tag{3.9}$$

Argue that this also shows the total spin to be a conserved quantity.

c. Verify that the generators (3.8) satisfy the $SO(3)$ algebra.

Despite the rotational invariance of $\hat{H}$, a ferromagnet has a spontaneous magnetic moment in the ordered phase. That is, below the so-called Curie temperature one has

$$< \hat{S}_z >= M_0 \neq 0, \tag{3.10}$$

where M_0 is the magnetization. This is the order parameter of the ferromagnetic phase: its value is non-zero in the ordered phase and zero in the symmetric one. The fact that we have chosen the spontaneous magnetization along the z-axis is of course entirely arbitrary. Experimentally one applies a small external field to align the spins. When the field is turned off again the magnetization stays oriented in the original field direction.

The occurrence of a spontaneous magnetization can easily be understood. Indeed, the ground-state energy of the system is minimal if all inner products contributing to the Hamiltonian (3.1) are positive with expectation value $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$. Thus the minimal ground-state energy at $T = 0$ is

$$E_0 =< 0_\uparrow | \hat{H} | 0_\uparrow >= -\tfrac{1}{4} \sum_{\alpha \neq \beta} J_{\alpha\beta} \tag{3.11}$$

for spins aligned in some arbitrary direction. In this state rotational symmetry is broken. However, the $SO(3)$ symmetry is not broken entirely since rotations around the magnetization axis are still symmetries of the ground-state. Therefore, in a ferromagnet the original symmetry group is broken down to $SO(2)$, which is isomorphic to the circle group $U(1)$. The broken symmetry corresponds to any rotation changing the direction of the magnetization. These rotations are given by the coset $R = SO(3)/U(1) = S^2$, i.e. the set of rotations represented by the two sphere. (Note that this set is not a group.) The consequences of such a symmetry breakdown will be further investigated below.

3.2 Effective Potential

It is obvious the the canonical density operator would yield a net magnetization zero, since all degenerate orientations of the spins are weighted equally. The appearance of a finite magnetization requires the state to transform non-trivially under rotations

$$\hat{\rho}' = \hat{U}^\dagger(\boldsymbol{\theta})\hat{\rho}\hat{U}\left(\boldsymbol{\theta}\right) \neq \hat{\rho}. \tag{3.12}$$

This is the manifestation of a broken symmetry below the critical temperature.

Exercise 3.2.

a. Use (3.5) to show that the rotational invariance of the canonical ensemble implies $< \hat{\mathbf{S}} >_c = 0$.

b. Conversely, show that a finite magnetization implies the breakdown of rotational invariance (3.12).

To lift the degeneracy of the different orientations in space, we may place the system in a small external field in the z-direction. The interaction of the spins with the field in the new Hamiltonian

$$\hat{H} \to \hat{H} - B\hat{S}_z \tag{3.13}$$

breaks the invariance with respect to rotations, since the perturbation is invariant only under the residual subgroup $U(1)$. The corresponding partition function is

$$Z(\beta, B, V) = \mathrm{Tr}\, \exp -\beta\left(\hat{H} - B\hat{S}_z\right). \tag{3.14}$$

This yields for the magnetization

$$M(B) = < \hat{S}_z >_B = \frac{1}{\beta}\frac{\partial \log Z}{\partial B}. \tag{3.15}$$

Now, we know that below the Curie temperature a zero-field magnetization M_0 remains after the external field is turned off. This may be understood as follows. Because of the symmetry-breaking term, the state with the magnetization along the B-axis, as compared with the state with opposite magnetization, has a relative probability

$$\frac{P-}{P+} = e^{-2\beta NSB}, \tag{3.16}$$

where S is the magnetization per spin and N the number of spins. In the thermodynamic limit $N \to \infty$, we have $P_- \to 0$ for any B. As $B \to 0$ the system is in the state with $M = M_0$. Thus, the zero-field state depends upon the history by which it is prepared. Also the crucial role of the thermodynamic limit is clear; if we keep N finite as $B \to 0$, we would get $P_+ = P_-$ and both states would be equally populated. We conclude that a non-vanishing magnetization density may be obtained by the following limiting procedure

$$m_0 = \lim_{B\to 0}\lim_{V\to\infty}\frac{1}{V} < \hat{S}_z >_B \tag{3.17}$$

which is called a quasi-average by Bogoliubov. The order of the two limits is crucial and cannot be interchanged.

It is useful to define a thermodynamic state function which depends on the magnetization, i.e. the order parameter, rather than the magnetic field. This function is obtained by defining the Legendre transform

$$\Gamma(\beta, M, V) = \Phi(\beta, B, V) + \beta MB. \tag{3.18}$$

Here $B = B(M)$ is a dependent variable that is obtained by inverting (3.15) to obtain the field in terms of the magnetization. It follows that Γ which is called the effective potential (or effective action), satisfies the reciprocity relation

$$\frac{\partial \Gamma}{\partial M} = \beta B. \tag{3.19}$$

The condition for symmetry breaking can now be formulated as the zero-field equation of state

$$\frac{\partial \Gamma}{\partial M} = 0. \tag{3.20}$$

Without explicit reference to the thermodynamic limit, and the preparation of the sample, the solutions of this equation represent all different configurations of the spontaneous magnetization. Above the Curie temperature the stable solution is the one for which the magnetization is zero. Below the transition temperature the stable solution is the one with a non-vanishing magnetization.

Exercise 3.3

a. Write down the Legendre transform relation between the entropy of the system and the effective potential Γ, and identify the primary independent thermodynamic variables appropriate to both S and Γ by writing out their variation.

b. Give the definition of the Helmholtz potential $\Psi = \Psi(T, M, V)$ and show that the variation is given by

$$\delta\Psi = -S\delta T + B\delta M - P\delta V. \tag{3.21}$$

c. Formulate the condition of symmetry breaking in terms of S and Ψ.

3.3 Bose-Einstein condensation

Let us now consider the model of an ideal Bose gas consisting of a number of N particles in a volume V characterized by their momentum $\mathbf{p}$ and energy $\varepsilon(\mathbf{p})$. According to chapter 2, exercise 2.6, this system is described by the Hamiltonian

$$\hat{H}_0 = \sum_{\mathbf{p}} \varepsilon\left(\mathbf{p}\right) \hat{a}^\dagger_{\mathbf{p}} \hat{a}_{\mathbf{p}}, \tag{3.22}$$

where the momentum-space occupation number operators satisfy the commutator relation (3.31). The total number operator

$$\hat{N} = \sum_{\mathbf{p}} \hat{a}^\dagger_{\mathbf{p}} \hat{a}_{\mathbf{p}} \tag{3.23}$$

is a conserved quantity, i.e. $\hat{N}$ commutes with $\hat{H}$.

In thermal equilibrium at temperature T the average number of particles occupying the quantum state $\mathbf{p}$ is given by the Bose-Einstein distribution function

$$< \hat{a}^{\dagger}_{\mathbf{p}} \hat{a}_{\mathbf{p}'} >= \frac{1}{\exp \beta \left(\varepsilon - \mu \right) - 1} \delta_{\mathbf{p}\mathbf{p}'}, \tag{3.24}$$

where μ is the chemical potential. We note that $\mu < 0$, or else some of the occupation numbers would be negative. For $\beta\mu$ very close to zero the occupation of the ground-state $\varepsilon, \mathbf{p} = 0$ can become macroscopic, that is, the ground-state density

$$n_0 = \frac{1}{V} < \hat{a}^{\dagger}_0 \hat{a}_0 > \cong -\frac{1}{V\beta\mu} \tag{3.25}$$

may contribute a finite fraction to the total particle density

$$n = \frac{1}{V} < \hat{N} >= n_0 + \lambda^{-3} G_{3/2} \left(\beta\mu \right). \tag{3.26}$$

In the second term the sum over momenta has been replaced by an integral over the energy by means of the substitution (2.42). In this term $\lambda = (2\pi/mT)^{1/2}$ is the thermal wavelength and G the Bose integral generally defined as

$$G_s \left(y \right) = \frac{1}{\Gamma \left(s \right)} \int_0^{\infty} dx \frac{x^{s-1}}{e^{x-y} - 1} \tag{3.27}$$

with $\Gamma(s)$ the gamma function. In the limit $y = 0$ the Bose-integral becomes equal to the Riemann ζ-function : $G_s(0) = \zeta \left(s \right)$.

The macroscopic occupation of the ground-state is called Bose-Einstein condensation. It occurs for temperatures and densities such that

$$n_0 = n - \lambda^{-3} \zeta \left(3/2 \right) \geq 0. \tag{3.28}$$

The equality defines a critical temperature (as a function of density) or a critical density (as a function of temperature). When the condensate density n_0 is expressed in terms of this critical temperature T_c, it is found to be a finite fraction of the total particle density

$$n_0 = n \left[1 - \left(\frac{T}{Tc} \right)^{3/2} \right]. \tag{3.29}$$

The condensate density, representing the density of particles with zero momentum, seems a natural choice for the order parameter in the case of Bose-Einstein condensation. However, a different definition will emerge when we analyze the relation with spontaneous symmetry breaking.

3.4 Broken Gauge Symmetry

Let us consider the expectation value of two field operators at two different spatial points. Using the Fourier expansion formula (2.38) we get

$$< \hat{\psi}^{\dagger}\left(\mathbf{x}\right)\hat{\psi}\left(\mathbf{x}'\right) >= \frac{1}{V}\sum_{\mathbf{p},\mathbf{p}'\neq 0} e^{i(\mathbf{p}+\mathbf{p}').\mathbf{v}} < \hat{a}^{\dagger}_{\mathbf{p}}\hat{a}_{\mathbf{p}'} > \\ + \frac{1}{V} < \hat{a}^{\dagger}_{0}\hat{a}_{0} >, \tag{3.30}$$

where the ground-state contribution has been separated from the other terms with $\mathbf{p}, \mathbf{p}' \neq 0$. For large values of the distance $\mathbf{v} = \mathbf{x} - \mathbf{x}'$, the first term vanishes on account of the Riemann-Lebesque theorem. However, the "off-diagonal" elements of the expectation value (3.30) remain finite under infinite separation in virtue of the second term:

$$\lim_{|\mathbf{v}|\to\infty} < \hat{\psi}^{\dagger}\left(\mathbf{x}\right)\hat{\psi}(\mathbf{x}') >= n_0, \tag{3.31}$$

where n_0 is the condensate density.

Exercise 3.4

a. Show that for a translationally invariant system the expectation value (3.30) only depends on the coordinate difference $\mathbf{v} = \mathbf{x} - \mathbf{x}'$.

b. Argue that the "diagonal" elements of expression (3.30) may be identified with the particle density

$$n =< \hat{\psi}^{\dagger}(\mathbf{x})\hat{\psi}(\mathbf{x}) > . \tag{3.32}$$

On the other hand, since we do not expect the expectation value of the field at point $\mathbf{x}$ to be influenced by a far away field at point $\mathbf{x}'$, we may assume the clustering property

$$\lim_{|\mathbf{v}|} < \hat{\psi}^{\dagger}\left(\mathbf{x}\right)\hat{\psi}\left(\mathbf{x}'\right) >=< \hat{\psi}^{\dagger}\left(\mathbf{x}\right) >< \hat{\psi}\left(\mathbf{x}'\right) > . \tag{3.33}$$

In combination with formula (3.33) this implies that a Bose-condensed system is characterized by off-diagonal long range order (ODLRO). It also implies that the expectation value of a field operator may be different form zero:

$$\left|< \hat{\psi} >\right|^2 = n_0. \tag{3.34}$$

This observation may be connected to the fact that the ground state of a Bose system is not gauge invariant.

To see this quite explicitly we recall the commutator relation

$$\left[\hat{N}, \hat{\psi}\left(\mathbf{x}\right)\right] = -\hat{\psi}\left(\mathbf{x}\right), \tag{3.35}$$

on account of which field operators acquire a phase factor under a gauge transformation:

$$e^{-i\lambda\hat{N}}\hat{\psi}\left(\mathbf{x}\right)e^{i\lambda\hat{N}}=e^{i\lambda}\hat{\psi}\left(\mathbf{x}\right). \tag{3.36}$$

Taking the expectation value we have to conclude that a non-vanishing value of the order parameter

$$\eta :=< \hat{\psi} >= \sqrt{n_0}e^{i\phi} \tag{3.37}$$

with ϕ a macroscopic phase angle, does not comply with a gauge invariant state.

Bose-Einstein condensation is the manifestation of broken gauge symmetry. This becomes particularly clear when we now discuss this phenomenon in analogy with the ferromagnetic case. To that purpose we introduce the operator

$$\hat{\eta}=\frac{1}{V^{1/2}}\hat{a}_0=\frac{1}{V}\int d^3x\hat{\psi}\left(\mathbf{x}\right), \tag{3.38}$$

which we couple to a fictitious symmetry breaking field ν in the Hamiltonian. The thermodynamic potential of the extended canonical ensemble

$$\Phi=-\log\ \mathrm{Tr}\ \exp-\beta\hat{H}-\propto\hat{N}-\beta V\left(\nu\hat{\eta}^{\dagger}+\nu^{*}\hat{\eta}\right) \tag{3.39}$$

can be calculated explicitly by diagonalizing the Hamiltonian. One finds

$$\frac{1}{V}\Phi\left(\nu,\nu^{*}\right)=\beta\frac{\left|\nu\right|^{2}}{\mu}-T\lambda^{-3}G_{5/2}\left(\beta\mu\right), \tag{3.40}$$

where the second term corresponds to the standard thermodynamic potential of the ordinary ideal Bose gas.

Exercise 3.5

a. Add a symmetry breaking term to the Hamiltonian according to

$$\hat{H}\rightarrow\hat{H}+V\left(\nu\hat{\eta}^{\dagger}+\nu^{*}\hat{\eta}\right), \tag{3.41}$$

Verify explicitly that this term breaks gauge symmetry.

b. Show that the new Hamiltonian can be diagonalized to the form

$$\hat{H}-\mu\hat{N}=\sum_{\mathbf{p}}\left(\varepsilon-\mu\right)\hat{b}^{\dagger}_{\mathbf{p}}\hat{b}_{\mathbf{p}}+V\left|\nu\right|^{2}/\mu \tag{3.42}$$

by the substitution $\hat{b}_{\mathbf{p}}=\hat{a}_{\mathbf{p}}-V^{1/2}(\nu/\mu)\delta_{\mathbf{p},0}$. Argue that this is a canonical transformation of the momentum operators.

Like in the magnetic example, the order parameter is obtained by differentiation with respect to the symmetry breaking "field":

$$<\hat{\eta}>=\frac{1}{\beta V}\frac{\partial\Phi}{\partial\nu^{*}}=\frac{\nu}{\mu}=\eta. \tag{3.43}$$

By differentiation with respect to $\propto= -\beta\mu$ we recover (3.34) for the particle density:

$$n = \frac{1}{V}\frac{\partial \Phi}{\partial \alpha} = \frac{|\nu|^2}{\mu^2} + \lambda^{-3} G_{3/2}\left(\beta\mu\right), \tag{3.44}$$

where the first term is equal to the condensate density $n_0 = |n|^2$. It is obvious that the condensate density vanishes in the limit $|\nu| \to 0$, except when μ is taken equal to zero at the same time. As we have seen in the magnetic case, the effective potential controls the values of the order parameter. In the present case we define this quantity as

$$\Gamma \equiv \Phi - \beta V \left(\nu\eta^* + \nu^*\eta\right) \tag{3.45}$$

satisfying the reciprocity relation

$$\frac{1}{\beta V}\frac{\partial \Gamma}{\partial \eta^*} = -\nu. \tag{3.46}$$

Substituting (3.40) and expressing the result in terms of the order parameter (3.43) we get

$$\frac{1}{V}\Gamma = \alpha\left|\eta\right|^2 - T\lambda^{-3} G_{5/2}\left(\beta\mu\right). \tag{3.47}$$

As we already expected, the zero-field equation admits two solutions: either $\eta = 0, \alpha \neq 0$, or $\eta \neq 0, \alpha = 0$. The last one describes the Bose condensed state.

Exercise 3.6

a. Rewrite the effective action in the form

$$\Gamma\left(\eta, \eta^*\right) = -\log\,\mathrm{Tr}\exp -\beta\hat{H} - \alpha\hat{N} - \beta V(\nu\delta\hat{\eta}^\dagger + \nu^*\delta\hat{\eta}). \tag{3.48}$$

b. Show that the equation

$$\Gamma\left(\eta_0, \eta_0^*\right) = \Phi\left(0, 0\right) \tag{3.49}$$

holds for any solution η_0 of the zero-field equation.

3.5 Ginzburg-Landau Theory

For a system with a realistic interaction between the particles, one cannot expect to be able to explicitly calculate the effective potential, like formula (3.47) for the ideal Bose gas. However, for the case of a second order transition the phenomenological approach proposed by Ginzburg and Landau in 1950 provides an effective alternative. The starting point is the general fact that in the less symmetric state a new macroscopic parameter η, called the order parameter, appears. This order parameter may be a scalar, a vector (as in ferromagnetic ordering), a complex number (as in Bose condensation), or some other quantity.

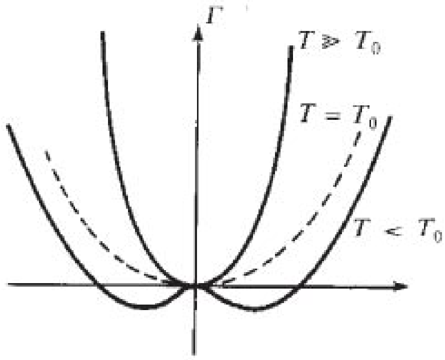

Figure 3.1: Effective potential

Let us assume, for simplicity's sake, that η is a scalar. We can then represent the effective potential as a function of η and the other thermodynamic variables $\Gamma = \Gamma(\alpha, \beta, V; \eta)$. Here it is to be remembered that the value of η must be determined from the extremum condition

$$\frac{\partial \Gamma}{\partial \eta} = 0, \tag{3.50}$$

whereas the other thermodynamic parameters may be specified arbitrarily. Thermodynamic stability requires the extremum to be minimum for $\eta = 0$ above the critical temperature T_c and $\eta \neq 0$ below T_c. Furthermore the effective potential must be a scalar function of the order parameter.

The continuity of a second-order transition allows η to become arbitrarily small near the transition point. It is reasonable therefore to assume that one may expand in powers of η:

$$\Gamma = \Gamma_0 + \alpha_I \eta + \alpha_2 \eta^2 + \alpha_3 \eta^3 + \alpha_4 \eta^4 + .. \tag{3.51}$$

The coefficients $\alpha_i = \alpha_i(T)$ are functions of T and the other thermodynamic parameters. We will assume that the ground-state of the system is degenerate with respect to $\eta \to -\eta$ (like in the two examples treated above). This implies that Γ cannot contain odd-order terms : $\alpha_1 = \alpha_3 = 0$.

The form of $\alpha_2(T)$ is chosen in such a way that above T_c the effective potential can only be minimum for $\eta = 0$. From the formulae

$$\frac{\partial \Gamma}{\partial \eta} = \eta \left(2\alpha_2 + 4\alpha_4 \eta^2 \right) = 0, \tag{3.52}$$

$$\frac{\partial^2 \Gamma}{\partial \eta^2} = 2\alpha_2 + 12\alpha_4 \eta^2 > 0, \tag{3.53}$$

we learn that we must require: $\alpha_2 > 0, T > T_c$. In the ordered phase, $\eta \neq 0$ must correspond to the stable state. Thus a sketch of Γ will look like in figure 1.

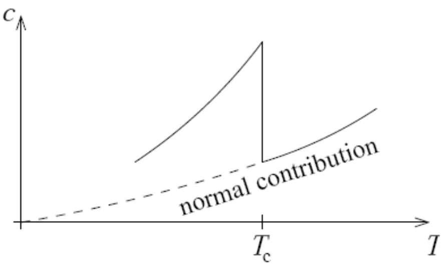

Figure 3.2: Behaviour of the heat capacity in the Ginzburg-Landau theory

We see that we must have $\alpha_2 < 0, T < T_c$, while $\alpha_2(T_c) = 0$. In order to have global stability, even at the transition point where $\eta = 0$, the coefficient α_4 must be positive.

The transition point is determined by the condition

$$\alpha_2(T) = 0. \tag{3.54}$$

If one assumes that this function is regular at T_c, it may be expanded as

$$\alpha_2(T) = \alpha(T - T_c) \tag{3.55}$$

with α some constant. The coefficient $\alpha_4(T)$ may in first order be replaced by $\alpha_4(T_c)$. Putting this into equation (3.52), we obtain

$$T > T_c \begin{cases} \eta = 0 \\ \Gamma = \Gamma_0 \end{cases}, \tag{3.56}$$

$$T < T_c \begin{cases} \eta^2 = \alpha\left(T_c - T\right)/2\alpha_4 \\ \Gamma = \Gamma_0 - \alpha^2\left(T - T_c\right)^2/2\alpha_4 \end{cases} \tag{3.57}$$

Thus below T_c the order parameter increases as $|T - T_c|^{\frac{1}{2}}$. Neglecting higher powers of η we find for energy

$$E = \frac{\partial \Gamma}{\partial \beta} = E_0 - \frac{\alpha^2 T^2\left(T_c - T\right)}{2\alpha_4}. \tag{3.58}$$

At the transition point this expression is continuous as it should be. However, the heat capacity is discontinuous

$$\Delta C = \frac{\alpha^2 T_c^2}{2\alpha_4}. \tag{3.59}$$

The jump has the shape of a greek lambda; it is therefore often called a λ-transition.

Near the transition point the minimum of Γ as a function of η becomes steadily flatter. As a consequence there is an increased sensitivity of a second-order phase transition to fluctuation effects for $T \to T_c$.

3.6 Goldstone Theorem

In the case of the Bose gas, we have seen that broken gauge symmetry entails the existence of long-range correlations below the critical temperature. In fact, this is a general characteristic of phase transitions accompanied by spontaneous symmetry breaking. In a system with only short-range forces, long-range order can only be understood if there is a mechanism that mediates information over long distances. In modern condensed matter physics this mechanism is pictured as the propagation of massless excitations through the system, the so-called Goldstone bosons. The number of independent Goldstone modes is the order of the remaining symmetry group of the system in the ordered phase (i.e. the set of transformations that leave the effective potential invariant but not the order parameter itself).

We will substantiate these statements by considering the general case of a set of symmetry generators $\hat{Q}_a, a = 1, 2 \ldots,$ satisfying the commutation relations

$$\left[\hat{Q}_{ab}, \hat{Q}_b\right] = i f^c_{ab} \hat{Q}_c, \tag{3.60}$$

where repeated indices are summed over their full range. The real coefficients f_{abc}, which are called structure constants, are antisymmetric in the indices a, b; there is no distinction between upper and lower indices. The operators $\hat{Q}_a$ are said to form a Lie-algebra. Given a Lie-algebra, there exists a Lie-group having these operators as its generators. In the two examples treated above the Lie-groups were the rotation group $SO(3)$ and the gauge group $U(1)$.

Exercise 3.7

a. Give the structure constants for the groups $SO(3)$ and $U(1)$.

b. Let $\hat{Y} = i\alpha_a \hat{Q}_a$. Show that the generators transform linearly

$$e^{-\hat{Y}} \hat{Q}_b e^{\hat{Y}} = \left(e^{i\alpha_a t_a}\right)_{bc} \hat{Q}_c \tag{3.61}$$

according to the adjoint representation defined by $(t_a)_{bc} = -i f_{abc}$. Use the expansion formula (2.51).

c. Write down the finite transformation formula corresponding to (3.35) in analogy with (3.61). Compare with (3.5).

Symmetry breaking is introduced by imagining that we have a theory with a set of operators

$$\hat{A}_i = \frac{1}{V} \int d^3x \hat{a}_i(\mathbf{x}) \tag{3.62}$$

which transform according to some representation T_a of the given Lie-algebra:

$$\delta_a \hat{A}_i = -i\left[\hat{Q}_a, \hat{A}_i\right] = i\left(T_a\right)_{ij} \hat{A}_j. \tag{3.63}$$

At this point we need te make a distinction between operators that commute with all generators, and operators that do not. If all observables belong to the former class, this gives rise to a superselection rule. In any case we will assume that the Hamiltonian in such an observable, i.e. $\hat{H}$ is invariant

$$\delta_a \hat{H} = -i \left[\hat{Q}_a, \hat{H} \right] = \frac{d}{dt} \hat{Q}_a = 0. \tag{3.64}$$

This implies that the generators

$$\hat{Q}_a(t) = \int d^3x \hat{q}_a(t, \mathbf{x}) \tag{3.65}$$

are conserved.

If now, below a critical temperature, the expectation value of equation (3.63) terns out to be non-zero, at least for some of the indices, then the state breaks the symmetry of at least one charge, i.e. $[\hat{\rho}, \hat{Q}_a] \neq 0$, and at least one of the operators (3.62) develops a non-vanishing expectation value

$$\eta_i = \frac{1}{V} \int d^3x < \hat{a}_i(\mathbf{x}) > \neq 0. \tag{3.66}$$

This identifies this expectation value as an order parameter: η_i is zero in the symmetric state and non-zero in the unsymmetrical one.

To obtain the Goldstone theorem we study the non-vanishing expectation value of (3.63) for a translationally invariant system. Picking the appropriate index we consider

$$\int d^3x < [\hat{q}_a(t, \mathbf{x}), \hat{a}_i(0)] > = -(T_a)_{ij} \eta_j \neq 0. \tag{3.67}$$

Note that in this case we can write $\eta_i =< \hat{a}_i(\mathbf{x}) >$. The time is arbitrary since the charge is conserved. Equation (3.67) is interesting because it implies that the so-called response function

$$\tilde{\chi}''(\omega, \mathbf{k}) = \tfrac{1}{2} \int d^4x e^{i\omega t - i\mathbf{k}.\mathbf{x}} < [\hat{q}_a(x), \hat{a}_i(0)] > \tag{3.68}$$

has a delta-peak in the long wave length limit:

$$\lim_{\mathbf{k} \to 0} \tilde{\chi}''(\omega, \mathbf{k}) = -\pi \delta(\omega) (T_a)_{ij} \eta_j. \tag{3.69}$$

This result signals the existence of a collective mode whose energy $\omega_a(\mathbf{k})$ goes to zero as $\mathbf{k} \to 0$, the so-called Goldstone mode. Such modes are identified by a peaked contribution to the response function (3.68) which converges to (3.69) in the limit $\mathbf{k} \to 0$. This peak could be a sharp excitation branch

$$\tilde{\chi}''(\omega, k) \propto \delta(\omega - \omega_a(\mathbf{k})) \tag{3.70}$$

with $\omega_a(\mathbf{k}) \to 0$ for $\mathbf{k} \to 0$. Or it could be a smooth peak with a width that narrows to zero as $\mathbf{k} \to 0$. In any case the number of these Goldstone modes is equal to the number of broken generators.

Goldstone bosons are not merely theoretical constructs since they can be detected experimentally. For example, in the Heisenberg ferromagnet the Goldstone excitations are known as magnons or spin waves with dispersion low $\omega \sim |k|^2$ for $\mathbf{k} \to 0$. The unusual temperature dependence of the heat capacity in the ferromagnet, $C_v \propto T^{3/2}$ for $T \to 0$, is due to these modes. In the free Bose gas the Goldstone excitations are the Bose particles themselves. The dispersion law is the same as above.

In conclusion one can say that spontaneous symmetry breakdown gives rise to low frequency Goldstone modes entailing long-range order. One condition is that no long-range forces are present. Such forces can conspire to prevent the occurrence of Goldstone modes. In particle theory this breakdown of the Goldstone theorem in gauge theories is called the Higgs mechanism [3].

Chapter 4

SUPERFLUIDITY AND SUPERCONDUCTIVITY

Superconductivity in metals and superfluidity in neutral systems are manifestations of intrinsically quantum mechanical collective behaviour. The general picture is based on the phenomenon of Bose condensation. Namely, below a critical temperature a finite fraction of all atoms begins to occupy a single quantum-mechanical state. This fraction increases to unity as the temperature decreases to zero. The atoms in this state become locked together in their motion and can no longer behave independently. Thus, for example, if the liquid flows through a narrow capillary, the processes of scattering of individual atoms by the walls are now totally ineffective, since all atoms must be scattered or none. The quantum-mechanical nature of the behaviour has other consequences. For example, if the liquid is placed in a doughnut-shaped container, the wave function must fit into the container, that is, there must be an integral number of wavelengths as one goes once around. Because of the fact that all condensed atoms are in the same state, the liquid can rotate only at certain special angular velocities.

A similar general picture is believed to apply for superconducting metals, except that the particles which undergo Bose condensation (and are therefore required to be bosons) are not individual electrons, but rather pairs of electrons which form in the metal, the so-called Cooper pairs. Something rather similar happens in ^{3}He, where the basic entities are also fermions. Here there is the further interesting feature that the fermion pairs which undergo Bose condensation have a rich and variable internal structure, which by the nature of the Bose condensation process must be the same for all pairs. This rich structure is reflected in the occurrence of a number of different superfluid phases. It is likely that the phenomenon of superfluidity also occurs in other systems of fermions, for example in the interior of a neutron star, although there is no firm evidence as yet.

The principles of superfluidity and superconductivity are described in many textbooks [8, 9, 10, 11]. Here we shall focus on those features which can be understood with little detailed calculation and which are in close formal analogy with our discussion of broken symmetry in the preceding chapter.

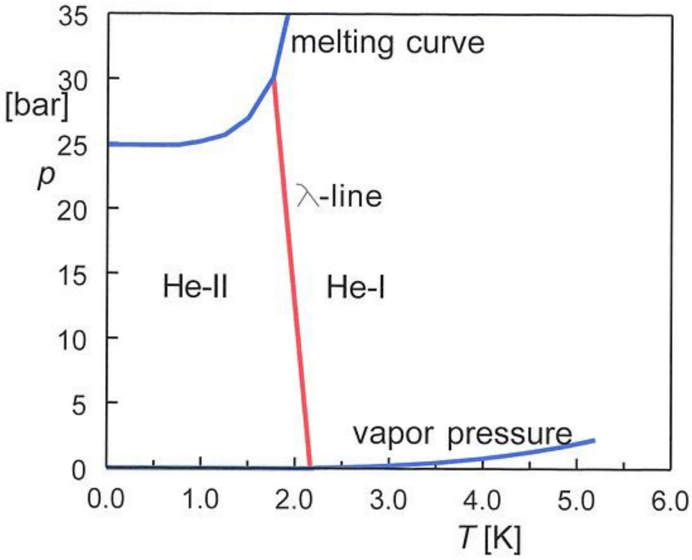

Figure 4.1: Phase diagram of ^{4}He

4.1 Liquid ^{4}He

From a microscopic point of view liquid Helium is the simplest of all condensed substances. Its atoms may be treated as structureless particles (except for the nuclear spin 1/2 carried by ^{4}He) interacting via an interatomic potential that is quite accurately known. The common isotope is ^{4}He consisting of atoms with zero total spin and obeying Bose statistics. The atoms of the rare isotope ^{3}He are fermions differing only by the addition of one neutron in the nucleus. As far is known, at low pressure both isotopes remain liquid down to absolute zero, where they solidify only under an applied pressure of ~ 25 Bar (^{4}He) and ~ 30 Bar (^{3}He). Since a classical system will always crystallize at sufficiently low temperature, liquid ^{3}He and ^{4}He are known as quantum liquids.

Under atmospheric pressure ^{4}He liquifies at 4.2 K and ^{3}He at 3.19 K. Immediately below their respective boiling points both ^{4}He and ^{3}He behave as ordinary liquids with a small viscosity. However at 2.17 K liquid ^{4}He undergoes a transition to a different phase, known conventionally as He II; see figure 1. This transition is signalled by a specific heat anomaly, whose characteristic shape has led to the name λ-point being given to the temperature at which it occurs.

The most spectacular property of He II is that it is superfluid. That is, it has been found (Kapitza, 1938) to flow through narrow capillaries and porous media without apparent friction. Being a fermionic system, liquid ^{3}He does not share this λ-transition. However, it has also found to have superfluid properties (Osheroff et al., 1972), albeit in the milli-Kelvin temperature range. This second-order transition is believed to be similar to the transition to the superconducting state in metals. We will leave a detailed discussion of ^{3}He for a later chapter.

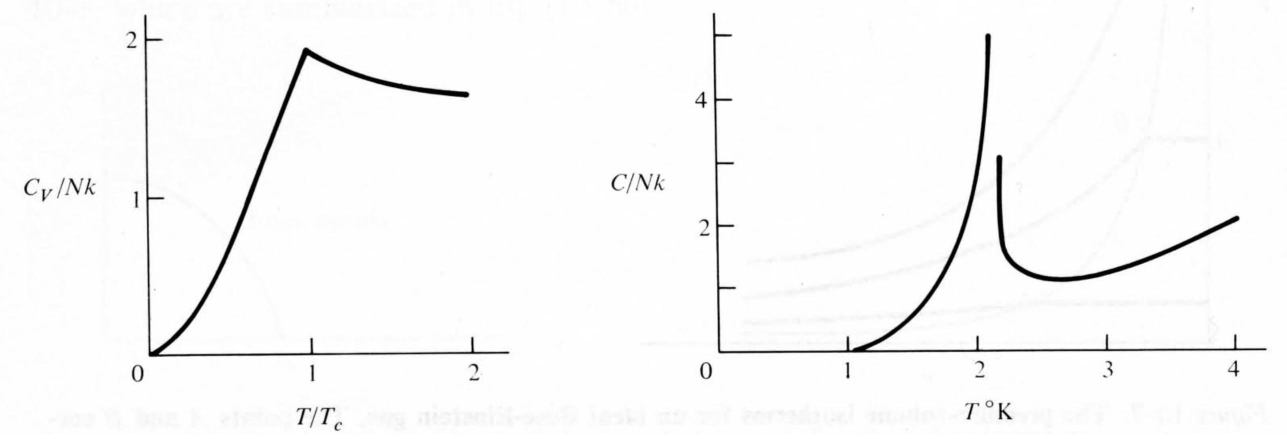

Figure 4.2: Specific heats of liquid ^{4}He and an ideal Bose-Einstein gas

Experiments to measure the viscous resistance to flow and the viscous drag on a body submerged in liquid ^{4}He have revealed that He II is capable of being non-viscous and viscous at the same time. This feature is explained by the two-fluid model first introduced by Tisza (1938). According to this model He II behaves as if it were a mixture of two liquids. One, the normal fluid, possesses an ordinary viscosity, and the other, the superfluid, is capable of frictionless flow past obstacles. It must be understood, however, that this is a purely phenomenological description, and that the fluid cannot in fact be physically separated into a normal and superfluid component.

One defines a mass density for the normal and superfluid components, ρ_n and ρ_s, respectively. The total mass density is the sum

$$\rho = \rho_n + \rho_s. \tag{4.1}$$

Likewise, one defines a local velocity for each component and a total mass current density

$$\mathbf{j} = \rho_n \mathbf{v}_n + \rho_s \mathbf{v}_s \tag{4.2}$$

This approach works well when the relative velocity $\mathbf{v}_n - \mathbf{v}_s$ is small. In a famous experiment devised by Andronikashvili (1946) the variation of ρ_n/ρ with the temperature can be measured. The ratio is unity at the λ-point. Below 1 K the liquid is almost entirely superfluid. It is further assumed that the entropy of He II is confined to the normal component: $S = S_n$, and that the normal component is responsible for the transport of heat. The superfluid carries no entropy and at absolute zero He II is entirely superfluid with zero entropy.

It is clear that the pure superfluid constitutes the ground state of He II. The analogy with the phenomenon of Bose-Einstein condensation for an ideal gas suggests that the superfluid fraction of He II may be identified with a Bose-Einstein condensate. This condensate is characterized by a delta-type of singularity in momentum space, in which a macroscopic fraction of the particles of the system is concentrated, and a condensate order parameter $\eta(\mathbf{x})$, also called condensate wave function, in coordinate space.

4.2 Superconductors

Superconductivity was discovered in 1911 by H. Kamerlingh Onnes in Leiden. What he observed was that the electrical resistance of various metals such as mercury, lead, and tin abruptly drops to zero in a small temperature interval at a critical temperature T_c, characteristic of the metal. Once set up, such currents have been observed to flow without measurable decrease for a year, and a lower bound of some 10^5 years for their characteristic decay time has been established. It is believed that the superconducting state is really a state of zero resistance. Thus, perfect conductivity is the first traditional hallmark of superconductivity.

The true nature of the superconducting state exhibits itself more clearly in the property of perfect diamagnetism discovered in 1933 by Meissner and Ochsenfeld. They found not only that a magnetic field is excluded from a superconductor, as might appear explained by perfect conductivity, but also that the field is expelled from an originally normal sample. This means that the state with the flux excluded is a true thermodynamic equilibrium state. Superconductivity is destroyed by a critical field H_c which is related to the free-energy difference between normal and superconducting states in zero field, the so-called condensation energy of the superconducting state:

$$\tfrac{1}{2}H_c^2(T) = f_n(T) - f_s(T). \tag{4.3}$$

Note that this condensation energy per unit volume is negative. The variation of H_c with temperature is described to within a few percent for all materials by

$$H_c\,(T) = H_c\left[1 - \left(\frac{T}{T_c}\right)^2\right]. \tag{4.4}$$

The value H_c of the critical field at zero temperature is typically some hundred Oersted. While the transition in a zero field at T_c is a virtually perfect second-order phase transition, the transition in the presence of a field is of first order, there being a discontinuous change in the thermodynamic state of the system and an associated latent heat.

In some metals (e.g. pure V and Nb) and most superconducting alloys the transition to the normal phase in a magnetic field is not immediate, but first the field penetrates through localized flux tubes parallel to the field. The core of these tubes is in the normal state. Outside these so-called vortices the system is still superconducting. The normal state is only restored completely until the upper critical field H_{c2} is reached. Superconductors with this behaviour are known as type-II.

The measurement of the electronic specific heat of superconductors by Corak et.al.(1954) showed that the heat capacity well below T_c was dominated by an exponential dependence

$$C_v = a\gamma T_c \exp -bT_c/T, \tag{4.5}$$

where γT is the normal-state electronic heat capacity, and $a \approx 10, b \approx 1,5$ numerical constants. Such an exponential dependence implies a minimum excitation energy per particle of $\Delta_0 \sim 1,5T_c$. This is one of the key predictions of the BCS theory set out in a

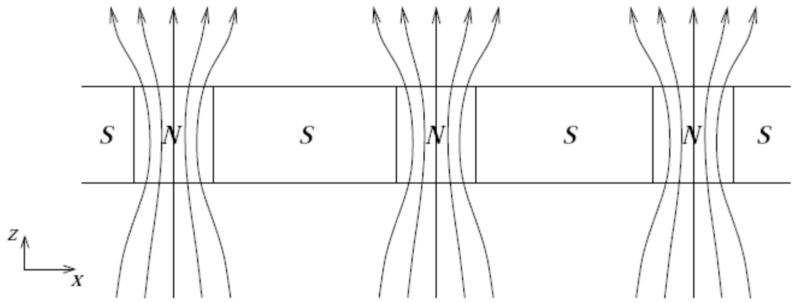

Figure 4.3: Flux tube in a type-II superconductor

fundamental paper by Bardeen, Cooper, and Schrieffer in 1957. The essential qualitative feature of the BCS-theory is that superconductivity results from an attractive interaction between electrons mediated by phonons (lattice vibrations). The effect of the interaction on two electrons is to bind them into an entity, called a Cooper pair, occupying states with equal and opposite momenta and spin. These Cooper pairs have a spatial extension $\xi_0 = av_F/T_c$, called the coherence length, where v_F is the Fermi velocity and a a numerical constant of order unity. The opposite spin means that the electrons are in a spin singlet ($\uparrow\downarrow$) state, and the pairing in superconductors is called s-wave.

The BCS state is made up of Cooper pairs which, roughly speaking comprise the superconducting charge carriers. This arrangement requires that some electron states just outside the normal Fermi surface are occupied, and some just inside are empty. The total energy of the BCS state is lower than that of the normal state, because the binding energy of the Cooper pair outweighs the increase in kinetic energy. The effect is that the particle energy

$$\varepsilon_{\mathbf{p}} = \sqrt{\Delta^2 + \left(\frac{\mathbf{p}^2}{2m} - \mu\right)^2} \tag{4.6}$$

cannot be less that the "gap" value Δ which is reached when $p = p_F$. In other words, the excited states of the system are separated from the ground state by an energy gap Δ. This $\Delta(T)$ was predicted to increase from zero at T_c to a limiting value such that $\Delta_0 = \Delta(T = 0) = 1.76T_c$, for $T << T_c$. The quantity 2Δ may be regarded as the binding energy of the Cooper pair which would have to be expended to break it up.

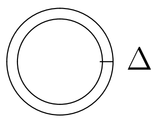

Figure 4.4: Gap around the Fermi sphere

It must be noted, however, although a typical feature of superconductivity, the existence of an energy gap is by no means necessary. This is shown in the occurrence of "gapless" superconductors with zero d.c. resistance.

Much of the physics of superconductivity can be understood on the basis of the existence of an order parameter $\eta(\mathbf{x})$ which has amplitude and phase, like for He II, and which maintains phase coherence over macroscopic distances. The condensate is analogous to, but not identical with, the familiar Bose-Einstein condensate, with Cooper pairs of electrons replacing the single bosons which condense in superfluid Helium.

4.3 Bose Fluid

Above we have established the idea that liquid ^{4}He below the λ-point possesses a condensate, that is, a macroscopically large number of particles occupying a single quantum state. We have also indicated that the superfluid properties reflect the macroscopic coherence of this state. In the following we give these ideas more substance by considering an interacting boson fluid as a model for ^{4}He. The particles in the system are described by operator fields that satisfy the canonical commutation relations

$$\left[\hat{\psi}(\mathbf{x}), \hat{\psi}^\dagger(\mathbf{x}')\right] = \delta(\mathbf{x} - \mathbf{x}'), \tag{4.7}$$

$$\left[\hat{\psi}(\mathbf{x}), \hat{\psi}(\mathbf{x}')\right] = \left[\hat{\psi}^\dagger(\mathbf{x}), \hat{\psi}^\dagger(\mathbf{x}')\right] = 0, \tag{4.8}$$

which characterize a system of bosons.

We assume that at the λ-transition gauge symmetry, generated by the number operator

$$\hat{N} = \int d^3x \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x}), \tag{4.9}$$

is broken. Thus, the condensed phase is characterized by a complex non-zero order parameter

$$\mu = < \hat{\psi}(\mathbf{x}) > = \sqrt{n_s}\varepsilon^{i\phi} \tag{4.10}$$

with a definite but arbitrary phase. The square modulus $n_s = |\eta|^2$ may be interpreted as the condensate density. The degenerate phase reflects the gauge symmetry in parallel with the ferromagnetic example, for which the magnitude of the magnetization is fixed but the orientation is arbitrary.

Exercise 4.1

a. Review the essentials of symmetry breaking. Follow the discussion in chapter 3.6 and specialize to the present case.

b. Identify the order parameter and the corresponding operator.

c. Argue that there is a Goldstone mode associated with the degenerate phase angle. Hint: discuss the operators $\left(\hat{\psi} + \hat{\psi}^\dagger\right)$ and $i\left(\hat{\psi} - \hat{\psi}^\dagger\right)$ separately.

The phase must be coherent over the whole system. The effect is to lock the condensate particles in a state of uniform motion. However, we will allow the phase to be slowly varying on a macroscopic scale as a function of position: $\phi = \phi(\mathbf{x})$. We may then define the quantity

$$\mathbf{g}_s = \eta^* \left(\overset{\leftrightarrow}{\nabla} /2i \right) \eta = n_s \nabla \phi \tag{4.11}$$

in analogy with the mass current in Schrödinger wave mechanics. The identification of this quantity with the superfluid mass current (or momentum) density

$$\mathbf{g}_s = \rho_s \mathbf{v}_s \tag{4.12}$$

makes the superfluid velocity proportional to the gradient of the phase of the order parameter

$$\mathbf{v}_s = \frac{1}{m} \nabla \phi. \tag{4.13}$$

The proportionality constant $m = \rho_s / n_s$ is the mass of the particles.

Broken gauge symmetry has already been discussed in some detail in the preceding chapter. Following the same line of reasoning, we construct the ensemble that lifts the degeneracy of the normal state by coupling the operator associated with the order parameter to an external source. In the present case the extended ensemble takes the canonical form

$$\Phi = -\log \mathrm{Tr} \exp -\hat{\Phi}, \tag{4.14}$$

but with the canonical exponent given by

$$\hat{\Phi} = \beta \hat{H} + \alpha \hat{N} + \int d^3x \left[\nu^* (\mathbf{x}) \hat{\psi} (\mathbf{x}) + \nu (\mathbf{x}) \hat{\psi}^\dagger (\mathbf{x}) \right]. \tag{4.15}$$

The sources play the role of Lagrange multipliers which must be chosen such that functional differentiation

$$\frac{\delta \Phi}{\delta \nu^* (\mathbf{x})} = < \hat{\psi} (\mathbf{x}) > \tag{4.16}$$

reproduces the actual value of the order parameter (4.10). As compared to the example of the ideal Bose gas, treated in section 3.4, we have generalized to a local formulation, in order to accommodate a spatial dependence of the order parameter. A trivial further difference is that we have absorbed a factor β in the external source field.

For (4.14), (4.15) to be acceptable as an equilibrium ensemble, it must have the property that expectation values of local operators $\hat{a}(\mathbf{x})$ are space independent:

$$< [\mathbf{P}, \hat{a} (\mathbf{x})] >= 0. \tag{4.17}$$

Here $\hat{\mathbf{P}}$ is the momentum operator of the system; see (2.3.8). This seems to present a problem because the above ensemble breaks translational invariance if the sources are not constant in space. However, for local gauge invariant operators, which constitute the observables of the system, it is obvious that we may rewrite (4.17) as

$$< \left[\hat{\mathbf{P}} - \mathbf{p} \hat{N}, \hat{a} (\mathbf{x}) \right] >= 0, \tag{4.18}$$

for arbitrary values of the parameter $\mathbf{p}$.

The physical meaning of the momentum $\mathbf{p}$ will become clear shortly. To that order we consider the equivalent condition

$$\left[\hat{\mathbf{P}} - \mathbf{p}\hat{N}, \hat{\Phi}\right] = 0. \tag{4.19}$$

By construction the number operator does not commute with $\hat{\Phi}$, as given in (4.15), and we find that the sources must satisfy the spatial homogeneity condition

$$(i\nabla + \mathbf{p})\, \nu\,(\mathbf{x}) = 0. \tag{4.20}$$

Writing $\nu = |\nu|\, e^{i\lambda}$, where $|\nu|$ is a constant, we obtain the solution

$$\lambda\,(\mathbf{x}) = \mathbf{x} \cdot \mathbf{p} + \lambda\,(0)\,. \tag{4.21}$$

The last term is an arbitrary constant. Without loss of generality it can be taken to be zero, because a constant phase can always be absorbed in the definition of the field operators.

We will now show that the phase of the external source (4.21) is equal to the phase of the order parameter. We start from the equation

$$< \left[\hat{\mathbf{P}} - \mathbf{p}\hat{N}, \hat{\psi}\,(\mathbf{x})\right] >= 0 \tag{4.22}$$

which is a direct consequence of condition (4.19). The known effect of the operators on $\hat{\psi}$ gives us the equation

$$(i\nabla + \mathbf{p})\, \eta\,(\mathbf{x}) = 0, \tag{4.23}$$

which is identical to (4.20). Hence we conclude, that apart from a trivial constant, the phases $\lambda(\mathbf{x})$ and $\phi(\mathbf{x})$ are equal, and we shall make no distinction between them in the following. We also obtain from (4.21)

$$\mathbf{g}_s = \mathbf{p} n_s. \tag{4.24}$$

This equation means that the condensate state has momentum $\mathbf{p}$. In other words, a macroscopically large fraction of the particles is in the state of momentum $\mathbf{p}$. The superfluid current is thus equated with the motion of the condensate.

Exercise 4.2

a. Derive equation (4.20) by explicit calculation of $\left[\hat{N}, \hat{\Phi}\right]$ and $\left[\hat{\mathbf{P}}, \hat{\Phi}\right]$.

b. Demonstrate that (4.22) implies that $< \hat{a}_{\mathbf{p}'} >\neq 0$ if and only if $\mathbf{p}' = \mathbf{p}$.

c. Make use of the result (4.21) to show the equilibrium condition essentially reduces the ensemble (4.15) to the form (5.12) of the preceding chapter.

4.4 Thermodynamics

It is convenient to reexpress the ensemble in a reference frame where the superfluid velocity is zero. We do this by introducing the unitary operator

$$\hat{U}_\phi = \exp -i \int d^3x \phi\left(\mathbf{x}\right) \hat{n}\left(\mathbf{x}\right), \tag{4.25}$$

where

$$\hat{n}\left(\mathbf{x}\right) = \hat{\psi}^\dagger\left(\mathbf{x}\right) \hat{\psi}\left(\mathbf{x}\right) \tag{4.26}$$

is the local number density operator. On account of the commutation relations (4.7), (4.8) the operator (4.25) induces a local gauge transformation on the fields:

$$\hat{U}_\phi \hat{\psi}\left(\mathbf{x}\right) \hat{U}_\phi^\dagger = e^{i\phi(\mathbf{x})} \hat{\psi}\left(\mathbf{x}\right). \tag{4.27}$$

We make use of this gauge transformation to eliminate the phase from the linear gauge breaking term in the canonical operator (4.15):

$$\hat{\Phi}' = \hat{U}_\phi \hat{\Phi} \hat{U}_\phi^\dagger = \beta \hat{H}' + \alpha \hat{N} + |\nu| \int d^3x \left[\hat{\psi}\left(\mathbf{x}\right) + \hat{\psi}^\dagger\left(\mathbf{x}\right)\right]. \tag{4.28}$$

However, the phase has not entirely disappeared, since we find it back in the transformed Hamiltonian

$$\hat{H}' = \int d^3x \left[\hat{e} + \hat{\mathbf{j}} \cdot \nabla\phi + \frac{1}{2m} \hat{\eta} \left(\nabla\phi\right)^2\right], \tag{4.29}$$

where $\hat{e}(\mathbf{x})$ is the local energy density operator and

$$\hat{\mathbf{j}}\left(\mathbf{x}\right) = \frac{1}{m} \hat{\psi}^\dagger\left(\mathbf{x}\right) \left(\overleftrightarrow{\nabla}/2i\right) \hat{\varphi}\left(\mathbf{x}\right) \tag{4.30}$$

the current density operator. In deriving formula (4.29) we have used the expansion formula (2.51) and the commutator relations (2.23) and (2.25). We observe that the new Hamiltonian is not a function of the phase itself, but of its gradient, which by definition is the momentum of the particles in the superfluid state: $\nabla\phi = \mathbf{p} = m\mathbf{v}_s$.

Exercise 4.3

a. Check that the transformation removes the phase of the order parameter $< \hat{\psi}\left(\mathbf{x}\right) >' = \sqrt{n_s}$. The prime indicates that the expectation value has to be taken with respect to the ensemble with canonical operator (4.28).

b. Argue that the thermodynamic potential (4.14) is invariant: $\Phi' = \Phi$.

c. Verify the results

$$\hat{n}'\left(\mathbf{x}\right) = \hat{n}\left(\mathbf{x}\right), \tag{4.31}$$

$$\hat{\mathbf{j}}'\left(\mathbf{x}\right) = \hat{\mathbf{j}}\left(\mathbf{x}\right) + \mathbf{v}_s \hat{n}\left(\mathbf{x}\right), \tag{4.32}$$

by applying the transformation (4.25) to the particle density (4.26) and the current density (4.30).

Since the superfluid velocity is constant, we may also write (4.29) as

$$\hat{H}' = \hat{H} + \mathbf{v}_s \cdot \hat{\mathbf{P}} + \tfrac{1}{2} m \mathbf{v}_s^2 \hat{N}. \tag{4.33}$$

Here $\hat{N}$ is the total number operator (4.8) and $\hat{\mathbf{P}}$ the total momentum operator (2.34). In fact, what we have derived here is the transformation law of the Hamiltonian under a Galilean transformation to a reference frame moving with velocity $\mathbf{v} = \mathbf{v}_s$ with respect to the laboratory frame. The corresponding unitary operator is

$$\hat{U}_{\mathbf{v}} = e^{-i\mathbf{v}\cdot\hat{\mathbf{G}}} \tag{4.34}$$

with boost generator

$$\hat{G} = m \int d^3x \, \mathbf{x} \, \hat{n}\left(\mathbf{x}\right). \tag{4.35}$$

One may verify that this definition is consistent with the basic algebra

$$\left[\hat{G}_i, \hat{H}\right] = i\hat{P}_i \tag{4.36}$$

$$\left[\hat{G}_i, \hat{P}_j\right] = iM\delta_{ij} \tag{4.37}$$

of the Galilean group. The constant M is the total mass of the system.

Exercise 4.4

a. Derive the commutator algebra for the Galilean group using the commutation relations given in chapter 2.

b. Check the transformation formula (4.33).

c. Consider the three quantities $< \hat{\mathbf{j}}' >'$, $< \hat{\mathbf{j}}' >$ and $< \hat{\mathbf{j}} >'$ involving the current density operator (4.30). Which of these represents the current density in the moving frame?

The effect of the Galilean transformation is to introduce the overall translational motion and kinetic energy in the Hamiltonian (4.33), and thereby in the canonical operator (4.28). The thermodynamic potential, which is an invariant, is seen to be a scalar function of the thermodynamic parameters α, β, the superfluid momentum $\mathbf{p}$, and the volume V: $\Phi = \Phi(\alpha, \beta, \mathbf{p}^2, V)$. Differentiation yields

$$\frac{1}{V}\frac{\partial \Phi}{\partial \alpha} = < \hat{n} >' = n, \tag{4.38}$$

$$\frac{1}{V}\frac{\partial \Phi}{\partial \beta} = < \hat{e}' >' = e, \tag{4.39}$$

$$\frac{1}{V}\frac{\partial \Phi}{\partial \mathbf{p}} = \beta < \hat{\mathbf{j}}' >' = \beta \mathbf{j}. \tag{4.40}$$

Here use has been made of the results (4.31) and (4.32). Recalling the connection $\beta P =$ - Φ/V, we obtain the fundamental thermodynamic relation

$$\delta\left(\beta P\right) = -n\delta\alpha - e\delta\beta - \beta\mathbf{j}\cdot\delta\mathbf{p} \tag{4.41}$$

which represents the second law of thermodynamics for a superfluid.

Exercise 5.5

a. Argue that the current density $\mathbf{j}$ is proportional to $\mathbf{v}_s$.

b. Derive the Gibbs relation $T\delta s = \delta e - \mu\delta n - \mathbf{v}_s\cdot\delta\mathbf{g}_s$ for a superfluid.

4.5 Cooper Pairing

Many metals are able to conduct an electric current without any resistance when they are cooled below a characteristic temperature. The transition from the normal state to the superconducting state is a phase transition of second order, characterized by the fact that the heat capacity of the metal has a discontinuity at the transition temperature. Again this is explained to be a consequen of the broken $U(1)$ gauge symmetry of the Hamiltonian. However, electrons are not bosons but fermions described by field operators $\hat{\psi}_\sigma\left(\mathbf{x}\right)$, with spin state up ($\sigma =\uparrow$) or down ($\sigma =\downarrow$), satisfying the anti-commutation relations

$$\left[\hat{\psi}_\sigma\left(\mathbf{x}\right), \hat{\psi}^\dagger_{\sigma'}\left(\mathbf{x}'\right)\right]_+ = \delta_{\sigma\sigma'}\delta\left(\mathbf{x}-\mathbf{x}'\right), \tag{4.42}$$

$$\left[\hat{\psi}_\sigma\left(\mathbf{x}\right), \hat{\psi}_{\sigma'}\left(\mathbf{x}'\right)\right]_+ = \left[\hat{\psi}^\dagger_\sigma\left(\mathbf{x}\right), \hat{\psi}^\dagger_{\sigma'}\left(\mathbf{x}'\right)\right]_+ = 0. \tag{4.43}$$

In terms of these fields the electron charge density and corresponding current density are given by

$$\hat{q}\left(\mathbf{x}\right) = e\sum_\sigma \hat{\psi}^\dagger_\sigma\left(\mathbf{x}\right)\hat{\psi}_\sigma\left(\mathbf{x}\right), \tag{4.44}$$

$$\hat{\mathbf{j}}\left(\mathbf{x}\right) = -\frac{e}{2m}\sum_\sigma\left[i\psi^\dagger_\sigma\left(\mathbf{x}\right)\nabla\hat{\psi}_\sigma\left(\mathbf{x}\right) + h.c.\right], \tag{4.45}$$

where e and m are the electron charge and mass, respectively. Charge and current density $\hat{j}^\mu = (\hat{q}, \hat{\mathbf{j}})$ satisfy the continuity equation

$$\partial_\mu \hat{j}^i\left(x\right) = 0, \tag{4.46}$$

which comprises the conservation of charge

$$\hat{Q} = \int d^3x\,\hat{q}\left(x\right) \tag{4.47}$$

in local form.

The Pauli principle as expressed by

$$\hat{\psi}_\sigma(\mathbf{x})\,\hat{\psi}_\sigma(\mathbf{x}) = 0, \tag{4.48}$$

forbids more than one electron from condensing into the same quantum state. Therefore, Bose-Einstein condensation of electrons is not physically possible. However, if the electrons were to form pairs, i.e. composite entities having boson properties, there is no contradiction in assuming that these pairs may accumulate in the same macroscopic state. It was shown in 1956 by Cooper that the effective attraction between electrons near the Fermi surface, due to electron-phonon interaction, must lead to bound states of electrons, regardless of how weak the attraction may be. With this idea as a starting point, it has been possible to construct a successful theory of superconductivity (Bardeen, Cooper, Schrieffer, 1957). In this theory a superconductor is characterized by a non-vanishing value of the electron-pair amplitude

$$F_{\sigma\sigma'}(\mathbf{x}-\mathbf{x}') =< \hat{\psi}_\sigma(\mathbf{x})\,\hat{\psi}_{\sigma'}(\mathbf{x}') >\neq 0. \tag{4.49}$$

In the homogeneous problem (i.e. in the absence of an external field), the expectation value depends only on the coordinate difference. Note that like in the Bose fluid, the state cannot be gauge invariant.

Two particles with spin 1/2 can pair in a singlet state with total spin $S = 0$, or in a triplet state with total spin $S = 1$ and spin projections $S_z = 0, \pm 1$. If we assume spherical symmetry, the electrons can only form pairs with opposite spins. In this case of so-called s-wave pairing, we need only consider

$$F(|\mathbf{x}-\mathbf{x}'|) =< \hat{\psi}_\uparrow(\mathbf{x})\,\hat{\psi}_\downarrow(\mathbf{x}') > . \tag{4.50}$$

This function describing the correlation between two electrons has a spatial range ξ_0, called the coherence length, and falls of rapidly beyond. By relating this length to the smallest size wave packet the electrons can form, one arrives at the estimate

$$\xi_0 = a\frac{v_F}{T_c}, \tag{4.51}$$

where $v_F = p_F/m$ is the Fermi velocity and where a is a numerical constant for which the BCS-theory gives the value $a = 0.18$. For real superconductors the order of magnitude of ξ_0 is 10^{-4} cm, much larger that the interparticle distance.

To within a constant factor the function $F(v), v = |\mathbf{x}-\mathbf{x}'|$, may be regarded as the wave function of a bound pair of particles relative to its centre of mass. The normalization

$$\int d^3v\,|F(v)|^2 = n_c, \tag{4.52}$$

therefore has an interpretation as the density of pairs. Obviously the quantity $|F(0)|^2\xi_0^3$ is of the same order of magnitude. This suggests that we define the order parameter for a superconducting system according to

$$\eta = \frac{\sqrt{n_c}}{|F(0)|} < \hat{\psi}_\uparrow(\mathbf{x})\,\hat{\psi}_\downarrow(\mathbf{x}) > \tag{4.53}$$

as the local product of two electron operators with opposite spins. This order parameter characterizes the simplest (BCS) type of superconductor with s-wave pairing. By definition the normalization $|\eta|^2 = n_c$ is the density of the Cooper pairs.

The order parameter (4.53) is a complex number with many formal properties in common with the order parameter describing a Bose fluid. A spatial dependence may be introduced by writing

$$\eta(\mathbf{x}) = |\eta| \, e^{2ie\phi(\mathbf{x})}. \tag{4.54}$$

What we assume here is that all quantities vary only slightly over distances of order ξ_0. This is called the London limit.

The phase is written in the particular form $2e\phi(\mathbf{x})$ because of the transformation properties of the order parameter under gauge transformations (see exc. 6). As we have seen, a space dependent phase gives rise to a supercurrent, which in the case of a superconductor, is an electric current. On account of the Maxwell equations such a current is coupled to a magnetic field. Hence, superconductivity cannot be discussed without taking electromagnetism into account. This will be the subject of the next section.

Exercise 4.6

a. Show the order parameter to transform according to

$$\eta \to \eta e^{2ie\phi} \tag{4.55}$$

under a gauge transformation generated by the charge (4.47).

b. Verify that the "covariant derivative"

$$D\eta = (\nabla - 2ie\mathbf{A})\,\eta \tag{4.56}$$

transforms in the same manner as η provided the field $\mathbf{A}$ is shifted according to the rule $\mathbf{A} \to \mathbf{A} + \nabla\phi$.

4.6 London equations

The electrodynamic properties of superconductors give the superfluidity of electrons in metals its unique interest. To investigate these properties we shall assume that an external field is coupled to the electrons. We choose a gauge in which the scalar potential vanishes. The vector potential $\mathbf{A}$ then gives the electric and magnetic fields according to

$$\mathbf{E} = -\partial_t \mathbf{A}, \tag{4.57}$$

$$\mathbf{B} = \nabla \wedge \mathbf{A}. \tag{4.58}$$

In analogy with the superfluid mass current (4.11) we define the electric supercurrent for a particle of mass 2m and charge 2e as

$$\mathbf{J}_s = \frac{e}{m}\eta^* \left(\overleftrightarrow{\nabla}/2i\right)\eta = \frac{(2e)^2}{2m}|n|^2 \nabla\phi. \tag{4.59}$$

As is well known, the coupling to an electromagnetic field arises from the requirement of local gauge invariance. This amounts to the replacement of the ordinary derivatives by the appropriate covariant derivative (see exc. 6). Performing this replacement in (4.59) we obtain

$$\mathbf{J}_s = \frac{2e^2}{m} |\eta|^2 \left(\nabla\phi - \mathbf{A}\right), \tag{4.60}$$

Thus a constant vector potential, which is not accompanied by an electric field, will nevertheless induce a finite current. Conversely, if no electric field is applied, a constant current is maintained: $\partial_t \mathbf{J} = 0$. This is superconductivity.

The phase of the order parameter may be eliminated by changing the gauge of the vector potential. Then equation (4.60) reads

$$\mathbf{J}_s = -m_A^2 \mathbf{A}, \tag{4.61}$$

which is known as London's equation.The gauge of $\mathbf{A}$ is specified by requiring $\nabla \cdot \mathbf{A} = 0$ so that the law of charge conservation $\nabla \cdot \mathbf{J}_s = 0$ is satisfied. The proportionality factor

$$m_A^2 = \frac{2e^2}{m} |\eta|^2 = 2\omega_p^2 \frac{n_c}{n}, \tag{4.62}$$

where $\omega_p^2 = en^2/m$ is the square of the ordinary electronic plasma frequency, has the dimension of a mass squared. Obviously it vanishes at the critical temperature. The occurrence of this mass may be seen as an instance of the Higgs mechanism: in a system with a broken symmetry a gauge boson, i.e. the photon in the case of electromagnetism, becomes massive.

In static situations the photon mass effective reduces the range of the electromagnetic interaction, i.e. its inverse $\lambda_L = m_A^{-1}$ acts as a screening length. The result is that a magnetic field is exponentially screened from the interior of a superconductor, i.e. the Meissner effect. This phenomenon of perfect diamagnetism was discovered by Meissner and Ochsenfeld in 1933. The London equation (4.60) provides the explanation. Indeed, taking the curl of this equation

$$\mathbf{B} + \lambda_L^2 \nabla \wedge \mathbf{J}_s = 0, \tag{4.63}$$

and combining this with the curl of the Maxwell equation

$$\nabla \wedge \mathbf{H} = \nabla \wedge \mathbf{B} - \mathbf{J}_s = 0, \tag{4.64}$$

we obtain after eliminating the current:

$$\lambda_L^2 \nabla^2 \mathbf{B} = \mathbf{B}. \tag{4.65}$$

The length λ_L is called the screening length or London penetration length. For a large enough sample the flux density decays from its external value to zero in the penetration region which is typically of the order 10^{-5} cm.

Exercise 4.7

a. Assume that a superconductor with a plane surface occupies the half-space $y > 0$ and is situated in a constant magnetic field H directed parallel to the z-axis. Determine the magnetic field $\mathbf{B}$.

b. Determine the supercurrent $\mathbf{J}_s$.

c. Explain the mechanism by which the flux is expelled.

The penetration depth of any superconducting material increases rapidly with temperature from some value $\lambda_L(0)$ at $T = 0$ to infinity as $T \to T_c$. Hence, there will always be a temperature interval in the neighbourhood of T_c where $\lambda_L(T) > \xi_0$. This is where the London approximation is valid. However, many of the known superconductors violate the condition for a pure London superconductor over almost the entire temperature range up to T_c. One then has to consider the non-local description as proposed by Pippard (1953). Unfortunately calculations become much more difficult in this case and we shall not discuss this any further.

Finally, we consider flux quantization. This is a striking conservation law implied by the generalized London equation (4.60). Integrating this equation around a closed path C lying wholly in the superconductor, we obtain

$$\oint_c d\mathbf{r} \cdot \left(\mathbf{A} + \lambda_L^2 \mathbf{J}_s\right) = \oint_c d\mathbf{r} \cdot \nabla\phi. \tag{4.66}$$

The first term on the left may be rewritten with the help of Stokes' theorem. If the order parameter is assumed to be single valued, the intergral on the right must be a multiple n of $2\pi/2e$:

$$\Phi = \oint_c d\mathbf{S} \cdot \mathbf{B} + \lambda_L^2 \oint_c d\mathbf{r} \cdot \mathbf{J}_s = \pm n \frac{\pi}{e}. \tag{4.67}$$

The left-hand side is London's fluxoid Φ which differs from the magnetic flux by an additional contribution arising from the induced supercurrent. The equation shows that ϕ is quantized in units of $\varphi_0 = \pi/e = 2.07 \times 10^{-7}$ gauss cm^2.

Exercise 4.8

a. Use the homogeneous Maxwell equation

$$\partial_t \mathbf{B} + \nabla \wedge \mathbf{E} = 0 \tag{4.68}$$

to show that Φ remains constant for all time.

b. Derive the London equations

$$\mathbf{E} = \frac{\partial}{\partial t} \lambda_L^2 \mathbf{J}_s, \tag{4.69}$$

$$\mathbf{B} = -\nabla \wedge \lambda_L^2 \mathbf{J}_s. \tag{4.70}$$

c. Conclude that Φ vanishes if the interior of C is wholly superconducting.

d. As a corollary of the previous conclusion, argue that Φ is the same for any path C' that can be deformed continuously into C.

If the sample of superconducting material is not simply connected, the integer n will be unequal to zero in general. Nonzero values of n, which is called a topological charge, also occur in type-II superconductors. The magnetic field then partially penetrates the sample in the form of thin filaments of flux. Each flux tube contains one single unit of flux φ_0. Within each filament the flux is high, and the material is not superconducting. Outside the core of the so-called Abrikosov vortex tubes the material is still superconducting and the field decays as described above. Circulating around each filament is a vortex of screening current.

Chapter 5

BCS THEORY

As understood today, superconductivity is explained by a spontaneous break down of electromagnetic gauge invariance. All important qualitative features, like the fact that electrical resistance is so low that currents can circulate for years, can be understood as exact consequences of this breakdown. However, to give a physical basis to the mechanism of symmetry breakdown, and as a starting point for approximate quantitative calculations, one needs a model. In this chapter we will study the microscopic model introduced by Bardeen, Cooper and Schrieffer (BCS) in 1957. This model has been highly successful in correlating and explaining the properties of simple superconductors in terms of a few experimental parameters.

In the BCS-model electrons appear explicitly, but it is assumed in advance that only electrons near the Fermi surface have an interaction, which is supposedly weak and attractive in nature. This effective electron-electron interaction arises from the exchange of phonons associated with the crystal lattice. The effects of this interaction on a normal solid are remarkably small and are described by simple replacing non-interacting particles by quasi-particles with slightly modified properties.

However, the introduction of an attractive interaction, no matter how weak, also leads to a bound state consisting of a pair of electrons at the Fermi surface with equal but opposite, momenta and spins. Once a macroscopic number of such Cooper pairs with a lower net energy appears, a description of the system in terms of single-particle states does no longer correspond to the state of lowest energy, and a transition to a new equilibrium state must take place. This qualitative different state cannot be obtained by a perturbative scheme which develops continuously from the original single particle states, and one has to include the possibility of pairing from the beginning.

5.1 Reference State

The BCS-theory starts from the following model Hamiltonian for an electron gas

$$\hat{H} = \sum_{\sigma} \int d^3x \left[\hat{\psi}^{\dagger}_{\sigma}(\mathbf{x}) \left(-\frac{\nabla^2}{2m} \right) \hat{\psi}_{\sigma}(\mathbf{x}) - \tfrac{1}{2} \lambda \hat{\psi}^{\dagger}_{\sigma}(\mathbf{x}) \, \hat{\psi}^{\dagger}_{-\sigma}(\mathbf{x}) \, \hat{\psi}_{-\sigma}(\mathbf{x}) \, \hat{\psi}_{\sigma}(\mathbf{x}) \right] \tag{5.1}$$

The electron field operators satisfy the standard anti-commutation relations. As shown by Cooper, the exchange of phonons leads to an effective attraction between electrons close to the Fermi surface. In the Hamiltonian (5.1) this interparticle potential has been approximated by an attractive delta-function-like potential with coupling constant $\lambda > 0$.

Before going on, it is important to emphasize that the BCS-theory serves as a model rather than as a valid microscopic theory. For example, what is missing is the repulsive Coulomb interaction between the electrons. The total interaction, which is the balance of the phonon-electron attraction and the Coulomb repulsion, may be either attractive or repulsive. In its general form, the problem of taking both interactions into account for actual models is very complicated, especially since real superconductors are anisotropic.

Exercise 5.1

a. Show that the interaction term of the BCS Hamiltonian (5.1) can be written in the quadratic form

$$\hat{V} = U \sum_{\sigma} \int d^3x \hat{n}_{\sigma}(\mathbf{x})\, \hat{n}_{-\sigma}(\mathbf{x}), \tag{5.2}$$

where $\hat{n}_{\sigma} = \hat{\psi}^{\dagger}_{\sigma}\hat{\psi}_{\sigma}$ (no summation).

b. For $U > 0$ this is known as the Hubbard interaction term. What is the sign of U in the present case?

c. Show that an equivalent representation is

$$\hat{V} = -\lambda \int d^3x \hat{\eta}^{\dagger}(\mathbf{x})\, \hat{\eta}(\mathbf{x}). \tag{5.3}$$

Identify the operators $\hat{\eta}$ and $\hat{\eta}^{\dagger}$.

The main reason why the BCS-model works is that it allows for the possibility for two electrons of opposite spins to form a self-bound Cooper pair. This results in the breaking of $U(1)$ gauge invariance and a non-zero value of the pair amplitude. In the BCS-theory it is customary to define the order parameter according to

$$\Delta(\mathbf{x}) = \lambda < \hat{\psi}_{\downarrow}(\mathbf{x})\, \hat{\psi}_{\uparrow}(\mathbf{x}) >= -\lambda < \hat{\psi}_{\uparrow}(x)\, \hat{\psi}_{\downarrow}(\mathbf{x}) >, \tag{5.4}$$

which is called the gap function and plays the role of an anomalous self-energy as we will explain in the sequel.

Let us now introduce the reference density operator to describe the superconducting state as

$$\hat{\rho} = \exp\left(\Phi_{\text{ref}} - \beta \hat{K}_{\text{ref}}\right), \tag{5.5}$$

$$\Phi_{\text{ref}} = -\log\left(\text{Tr}\exp -\beta \hat{K}_{\text{ref}}\right), \tag{5.6}$$

where the canonical operator is given by

$$\hat{K}_{\text{ref}} = \int d^3x \left[\hat{\psi}^{\dagger}_{\sigma}\left(-\frac{\nabla^2}{2m} - \mu\right)\hat{\psi}_{\sigma} - \nu \hat{\psi}^{\dagger}_{\uparrow}\hat{\psi}^{\dagger}_{\downarrow} - \nu^* \hat{\psi}_{\downarrow}\hat{\psi}_{\uparrow}\right], \tag{5.7}$$

with $\nu(\mathbf{x})$ a function to be determined. As we have discussed before such an ensemble explicitly breaks gauge invariance. No interaction other than the one with the source field $\nu(\mathbf{x})$ has been included. This approximation is based on the assumption that such terms would be the same in both normal and superconducting phases and do not affect the comparison between the two states.

To determine $\nu(\mathbf{x})$ we recall the Gibbs-inequality (1.21). Substituting (5.1) and (5.5) with (5.7) we obtain

$$\Phi\left[\nu, \nu^*\right] - \Phi_{eq} \geq 0, \tag{5.8}$$

where Φ_{eq} is the ordinary equilibrium thermodynamic potential and

$$\Phi\left[\nu, \nu^*\right] = \Phi_{\text{ref}} - \beta < \hat{K} - \hat{H} + \mu\hat{N} >_{\text{ref}} \tag{5.9}$$

a functional of ν and $\nu*$ corresponding to the thermodynamic potential of the reference state. Taking the definition of the gap function (1.4) into account, this expression may be rearranged in the form

$$\begin{aligned} \Phi\left[\nu, \nu^*\right] = \Phi_{\text{ref}} - \frac{\beta}{\lambda}\int d^3x \Big[\nu\Delta^* + \nu^*\Delta - |\Delta|^2 \\ - < \left(\lambda\hat{\psi}^\dagger_\uparrow\hat{\psi}^\dagger_\uparrow - \Delta^*\right)\left(\lambda\hat{\psi}_\uparrow\hat{\psi}_\uparrow - \Delta\right) >_{\text{ref}}\Big] \end{aligned} \tag{5.10}$$

The last term is negative definite and describes fluctuations of the order parameter. Because of the large number of particles involved, the fluctuations about the expectation value should be very small. In the BCS-theory these fluctuations are ignored. This mean field approximation breaks down only in a small region very close to the critical temperature, the so-called Ginzburg region, due to critical fluctuations.

Exercise 5.2

Let $\Phi[\hat{A}] = -\log Tr\exp -\hat{\beta}\hat{A}$ be the thermodynamic potential corresponding to the canonical operator $\hat{A}$. Then show that the Gibbs inequality can be rewritten in the form of the Bogoliubov-Peierls inequality

$$\Phi[\hat{A} + \hat{B}] \leq \Phi[\hat{A}] + < \hat{B} >_{\hat{A}} \tag{5.11}$$

valid for arbitrary Hermitian operators $\hat{A}$ and $\hat{B}$.

For the remainder we use the much simpler expression obtained from (5.10) by removing the last term representing the fluctuations. The scheme is now to find a best single-particle ensemble by minimizing this expression, regarding $\nu(\mathbf{x})$ as a trial function that has to be optimized. The functional differentiation of the first term at the right-hand side of (5.10) gives

$$\frac{\delta\Phi_{\text{eff}}}{\delta\nu^*} = -\beta < \hat{\psi}_\downarrow\hat{\psi}_\uparrow >_{\text{ref}}, \tag{5.12}$$

where the right-hand side is essentially the gap function as a functional of $\nu(\mathbf{x})$. For the variation of the potential (5.10), minus the fluctuations, we thus find

$$\delta\Phi = \frac{\beta}{\lambda}\int d^3x\,(\nu - \Delta)\delta\Delta^* + \text{c.c}, \tag{5.13}$$

which shows that Φ may be regarded as a functional of Δ and Δ^*. The minimum is reached for $\nu = \Delta$. This introduces selfconsistency into the theory because Δ now both determines and is determined by equation (5.12):

$$\frac{\lambda}{\beta} \frac{\delta \Phi_{\mathrm{ref}}}{\delta \Delta^* (\mathbf{x})} = -\Delta (\mathbf{x}) . \tag{5.14}$$

In this way we obtain the following minimized expression for the thermodynamic potential of the reference state:

$$\Phi \left[\bar{\Delta}, \bar{\Delta}^* \right] = \Phi_{\mathrm{ref}} - \frac{\beta}{\lambda} \int d^3x \left| \bar{\Delta} (\mathbf{x}) \right|^2 , \tag{5.15}$$

where $\bar{\Delta}(\mathbf{x})$ is a solution of the self-consistent gap-equation (5.14). From the Gibbs inequality (5.8) we know that this thermodynamic potential is always larger or equal to the true equilibrium thermodynamic potential. In fact, under fairly general conditions it can be shown that they are equal. This is the content of a theorem due to Bogoliubov jr (1966) which states that in the thermodynamic limit the minimum of the difference (5.8) converges to zero. The main step in the proof, which is too lengthy to reproduce here, is to derive an upper bound on the fluctuations. In a later section we will discuss a different approach which will make the mean-field character of the BCS-theory and the role of the fluctuations much more transparent.

5.2 Gap equation

For convenience we introduce the Nambu 2×2 matrix notation for the fields

$$\psi^\dagger = \left(\hat{\psi}^\dagger_\uparrow, \hat{\psi}_\downarrow \right), \; \hat{\psi} = \begin{pmatrix} \hat{\psi}_\uparrow \\ \hat{\psi}^\dagger_\downarrow \end{pmatrix} \tag{5.16}$$

The anticommutation relation they satisfy is

$$\left[\hat{\psi} (x) , \hat{\psi}^\dagger (\mathbf{x}') \right] = \mathbf{1} \delta (\mathbf{x} - \mathbf{x}') . \tag{5.17}$$

With the help of this notation we can rewrite the reference canonical operator as

$$\hat{K}_{\mathrm{ref}} = \int d^3x \hat{\psi}^\dagger (\mathbf{x}) \mathcal{E} \hat{\psi} (\mathbf{x}) , \tag{5.18}$$

where $\mathcal{E}$ is the 2×2 matrix operator

$$\mathcal{E} = \begin{pmatrix} \varepsilon (\mathbf{p}) - \mu & -\Delta \\ -\Delta^* & -\varepsilon (\mathbf{p}) + \mu \end{pmatrix} \tag{5.19}$$

with $\varepsilon(\mathbf{p}) = p^2/2m$ the kinetic energy. In deriving (5.18) we explicitly used the anti-commuting nature of the fields. One may note that the matrix $\mathcal{E}^2$ is diagonal

$$\mathcal{E}^2 = \begin{pmatrix} (\varepsilon - \mu)^2 + |\Delta|^2 & 0 \\ 0 & (\varepsilon - \mu)^2 + |\Delta|^2 \end{pmatrix} \tag{5.20}$$

This implies that the eigenvalues of E occur in pairs

$$E_{\pm} = \pm\sqrt{(\varepsilon-\mu)^2 + |\Delta|^2} = \pm E\left(\mathbf{p}\right). \tag{5.21}$$

Hence, the energy spectrum of the Fermi-excitations exhibits a gap, that is, the excitation energy cannot be less that $|\Delta|$. The gap value is reached for $\varepsilon = \mu$, which at low temperatures may be put equal to the Fermi energy $\varepsilon_F = \mu\,(T=0)$. The gap is qualitatively explained as the finite binding energy of the Cooper pair formed by two electrons close to the Fermi surface.

Exercise 5.3

Determine the eigenvalues of the matrix $\mathcal{E}$ by solving the secular equation

$$\det\left(\mathcal{E}^2 - \lambda^2\mathbf{1}\right) = 0. \tag{5.22}$$

Formally we may apply a similarity (canonical) transformation to the matrix $\mathcal{E}$ to bring it in diagonal form. The resulting expression for the reference thermodynamic potential then takes the form of partition function for an ideal gas of two types of particles with energies given by (5.21). Without further calculation we write down the explicit expression

$$\Phi_{\text{ref}} = -\sum_{\pm}\sum_{\mathbf{p}}\log\left(1+e^{-\beta E\pm}\right). \tag{5.23}$$

The reasoning applies for a constant gap, but a generalization to a gap function which depends on $|\mathbf{p}|$ can easily be incorporated.

Exercise 5.4

a. Consider the bilinear Hamiltonian operator

$$\hat{K}_0 = \sum_{ij}\hat{a}_i^\dagger\, t_{ij}\hat{a}_j, \tag{5.24}$$

where t_{ij} is an hermitian matrix, and $\hat{a}_i$ satisfies the standard canonical (anti-) commutation relations. Argue that this $\hat{K}_0$ can always be brought into the diagonal form $\hat{K}_0 = \sum_i \varepsilon_i\,\hat{a}_i^\dagger\hat{a}_i$.

b. Calculate the partition function

$$\log Z = \pm\sum_i\log\left(1\pm e^{-\beta\varepsilon_i}\right), \tag{5.25}$$

where each mode contributes an additive term.

Let us now consider the gap equation (5.14) for constant Δ, which we may assume to be real: $\Delta = |\Delta|$. Functional differentiation becomes ordinary differentiation which is easily performed. From (5.23) we find:

$$\frac{\partial \Phi_{\text{ref}}}{\partial \Delta} = -\beta \Delta \sum_{\mathbf{p}} \frac{\tanh \frac{1}{2}\beta E}{2E}. \tag{5.26}$$

Substituting this result in the gap equation and canceling the common factor Δ, we find

$$1 = \frac{\lambda}{(2\pi)^3} \int d^3 p \, \frac{\tanh \frac{1}{2}\beta E}{2\beta E}, \tag{5.27}$$

where we changed from summation to integration by the rule (2.42). The last equation is the BCS-gap equation which is a non-linear integral equation for the gap parameter as a function of temperature $\Delta = \Delta(T)$. One may note immediately that this equation would have no solution if $\lambda < 0$, i.e. in the case of repulsion, since the two sides would have opposite sign.

Since the general solution of the gap equation requires numerical methods we shall confine ourselves to some limiting behaviour. For that purpose it is convenient to change variables to $\xi = \varepsilon(\mathbf{p}) - \mu$ and to introduce the density of states according to the formal definition

$$\nu(\xi) = 2 \int \frac{d^3 p}{(2\pi)^3} \, \delta(\xi - \varepsilon(\mathbf{p}) - \mu). \tag{5.28}$$

When integrands are peaked near the Fermi surface, we may use the approximation $\nu(\xi) \cong \nu(0) =: \nu_F$. The symmetry of the integrand of (5.27) then allows us to write

$$1 = \lambda \nu_F \int_0^{\omega_D} d\xi \, \frac{\tanh \frac{1}{2}\beta E}{2E}. \tag{5.29}$$

The integral must be cut off at some value ω_D to render it convergent. In the present model the interaction with the crystal lattice leads to an attractive force between the electrons. Since the Debije energy ω_D is a measure for the inverse lattice spacing, this leads to the condition that only electrons with energies of thickness $2\omega_D$ about the Fermi surface participate. In all practical cases we have $\omega_D << \varepsilon_f$. Typical values are $\omega_D \sim 100K$ and $\varepsilon_F \sim 10.000K$.

Exercise 5.5

a. Calculate $\nu(\xi)$ for the present model.

b. Show that the density of states at the Fermi surface is given by $\nu_F = m p_F/\pi^2$ where p_F is the Fermi momentum.

In the zero-temperature limit equation (5.29) reduces to

$$1 = \lambda v_F \int_0^{\omega_D} \frac{d\xi}{2E}. \tag{5.30}$$

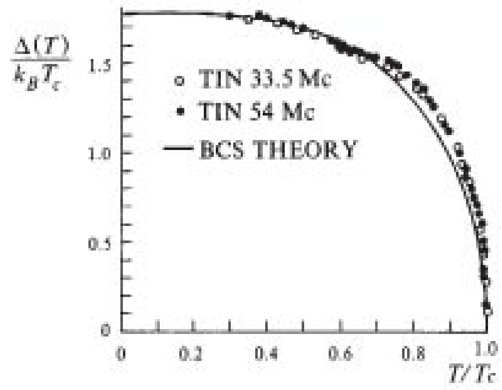

Figure 5.1: Temperature dependence of the energy gap in the BCS- theory

The integral is elementary and gives

$$\Delta(0) = \frac{\omega_D}{\sinh(2/\lambda\nu_F)}, \tag{5.31}$$

For many superconductors the dimensionless coupling constant $g = 1/2\lambda\nu_F$ is small: $g \cong 0.2 - 0.3$. In the weak-coupling limit we obtain

$$\Delta(0) = 2\,\omega_D e^{-\frac{1}{g}}, \tag{5.32}$$

which depends sensitively on the value of coupling constant. One may note that the point $g = 0$ is an essential singularity. This non-analyticity means that the above results can never be obtained by a perturbation expansion the small parameter g.

In the opposite limit $T \to T_c$ the gap vanishes by definition and we find

$$1 = g \int_0^{\omega_D} \frac{d\xi}{\xi} \tanh\frac{\xi}{2T_c}. \tag{5.33}$$

It is possible to solve this implicit equation for T_c (see e.g. reference [10]). The result is

$$\omega_D\, e^{-1/g}. \tag{5.34}$$

We see that T_c and the zero-temperature gap both depend in the same way on the coupling constant g. This dependence cancels in forming the ratio

$$\frac{2\Delta(0)}{T_c} = 3.52, \tag{5.35}$$

which is a universal constant independent of the material. Experimental results give reasonable agreement with this value.

The temperature dependence of the gap can be computed numerically. For weak coupling superconductors $\Delta(0) << \omega_D$, the ratio $\Delta(T)/\Delta(0)$ is a universal function determined by

$$\log\frac{\Delta(T)}{\Delta(0)} = -2\int_0^{\omega_D}\frac{d\xi}{E}\quad\frac{1}{e^{\beta E}+1}, \tag{5.36}$$

which decreases monotonically to zero at T_c, as shown in figure 1.

Near $T = 0$ the temperature variation is exponentially slow

$$\Delta(T) \approx \Delta(0) - \sqrt{2\pi\Delta(0)\,T}e^{-\Delta(0)/T}, \tag{5.37}$$

so that the hyperbolic tangent is nearly unity and insensitive to T. This means that Δ is nearly constant until a significant number of excitations is thermally excited. On the other hand, near $T_c, \Delta(T)$ drops to zero approximately as

$$\Delta(T) \approx \pi\left[\frac{8}{7\zeta()}\right]^{\frac{1}{2}}(T_c - T)^{\frac{1}{2}}. \tag{5.38}$$

The variation of the order parameter with the square root of $T_c - T$ is characteristic of all mean field theories.

Exercise 5.6

a. Derive (5.37) from (5.36). For details consult ref [10].

b. Near T_c expand directly in powers of Δ to prove (5.38).

5.3 Thermodynamic properties

For the subsequent calculations we start from the thermodynamic potential (5.15) specialized to the case of a constant gap

$$\Phi = \Phi_{\text{ref}} - \frac{\beta V}{\lambda}\Delta^2. \tag{5.39}$$

The first term is the thermodynamic potential (5.23) of the reference system, i.e. an ideal gas of fermion excitations (quasi particles) with energies $E_\pm = \pm E = [(\varepsilon-\mu)^2+\Delta^2]^{\frac{1}{2}}$. In the present uniform system the spatial integration merely introduces the volume factor V.

The entropy is obtained by differentiation

$$S = -\Phi - T\frac{\partial\Phi}{\partial T} = -\Phi_{\text{ref}} - T\frac{\partial\Phi_{\text{ref}}}{\partial T}. \tag{5.40}$$

The temperature dependence of the gap function can be ignored in the differentiation, since Φ is stationary with respect to variations $\delta\Delta$. Working out the right-hand side we obtain

$$S = -2\sum_{\mathbf{p}}\left[f\log f + (1-f)\log(1-f)\right], \tag{5.41}$$

where

$$f(E) = \frac{1}{e^{\beta E} + 1} \tag{5.42}$$

is the quasi-particle distribution function. As one could have expected, the expression is of the usual form for a free fermion gas.

Exercise 5.7

a. Check equation (5.40).

b. Derive equation (5.41). Useful identities are

$$\frac{\partial}{\partial \beta E} f = -f(1-f), \tag{5.43}$$

$$\log \frac{f}{1-f} = -\beta E. \tag{5.44}$$

Let us now first consider the heat capacity given by

$$C = \frac{T}{V}\frac{\partial S}{\partial T} = 2\frac{T}{V}\sum_{\mathbf{p}} \frac{\partial f}{\partial T} \log \frac{f}{1-f}. \tag{5.45}$$

Using (5.44) and changing from summation to integration, we get

$$C = \nu_F \int_{-\infty}^{\infty} d\xi E \frac{\partial f}{\partial T}. \tag{5.46}$$

In the limit $T \sim \xi \ll \Delta$, the quasi-particle energy may be approximated as $E \sim \Delta_0 + \frac{1}{2}\xi^2/\Delta_0$, where $\Delta_0 = \Delta(0)$, and the quasi-particle distribution as $f \sim \exp -E/T$. A simple integration gives the heat capacity in the superconducting phase as

$$C_s = \nu_F \sqrt{\frac{2\pi\Delta_0^5}{T^3}} e^{-\Delta_0/T}. \tag{5.47}$$

Thus, as $T \to 0$, the heat capacity decreases exponentially. This is a direct consequence of the presence of the gap in the energy spectrum.

Another interesting limit is near the transition temperature T_c. Then, as $\Delta(T) \to 0$, one can replace E by ξ in (5.46) after working out the temperature derivative:

$$C_n = \nu_F T \int_{-\infty}^{\infty} dx \frac{x^2 e^x}{(e^x + 1)^2} = \frac{1}{3}\pi^2 \nu_F T. \tag{5.48}$$

The second term is finite below T_c, where the temperature derivative is large. The discontinuity is readily evaluated as follows.

$$\Delta C = C_s - C_n = -\frac{1}{2}\nu_F \left.\frac{\partial \Delta^2}{\partial T}\right|_{T_c} \tag{5.49}$$

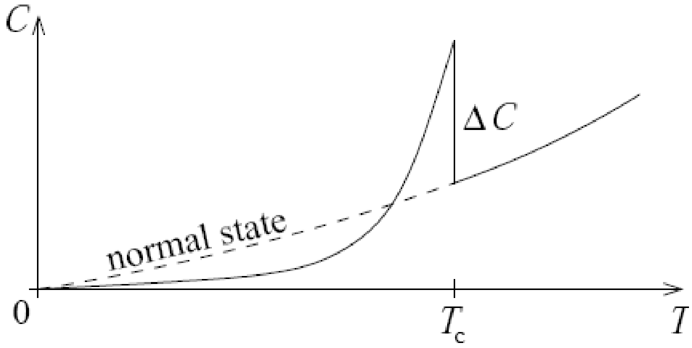

Figure 5.2: Heat capacity in the superconducting and normal states

Using now the approximate form (5.38) for $\Delta(T)$, we obtain

$$\Delta C = \frac{4\pi\nu_F}{7\zeta(3)} T_c = 4.7\nu_F T_c \tag{5.50}$$

The behavior of the heat capacity is shown in Figure 2.

We now wish to calculate the difference between the thermodynamic potential Φ_s in the superconducting state and the value Φ_n it would have in the normal state ($\Delta = 0$) at the same temperature. It is convenient to start from the formula

$$\frac{\partial\Phi}{\partial\lambda} = -\frac{\beta V}{\lambda^2}\Delta^2 \tag{5.51}$$

obtained from (5.39) by taking the derivative with respect to the coupling constant λ. We define $\Phi_n = \Phi(\lambda = 0)$. We then may write

$$\Phi_s - \Phi_n = \beta\nu_F V \int_0^g \Delta^2 d\left(\frac{1}{g'}\right), \tag{5.52}$$

where we changed to the coupling constant $g = \frac{1}{2}\lambda\nu_F$. At absolute zero $\Delta = \Delta_0$, and from (5.32)

$$\frac{d\Delta_0}{d\left(\frac{1}{g}\right)} = -\Delta_0. \tag{5.53}$$

Changing in (5.52) to an integration over Δ_0, we find the following expression for the difference between the thermodynamic potentials of the superfluid and normal system:

$$\Phi_s - \Phi_n = -\frac{1}{2}\beta\nu_F V \Delta_0^2. \tag{5.54}$$

The negative sign indicates that the normal state is unstable against the formation of Cooper pairs and that the superconducting state has indeed a lower thermodynamic potential. We can interpret expression (5.54) as the binding energy Δ_0 per pair multiplied by the number of pairs $\frac{1}{2}\nu_F\Delta_0$ per unit volume lying within the shell of thickness Δ_0 around the Fermi surface.

Let us now take the opposite case $T \to T_c$. We now differentiate (5.36) with respect to g, and find

$$\frac{7\zeta(3)}{4\pi^2T^2}\Delta d\Delta = \frac{d\Delta_0}{\Delta_0} = -d\left(\frac{1}{g}\right). \tag{5.55}$$

We substitute this into (5.52)

$$\Phi_s - \Phi_n = -\frac{7\zeta(3)}{8\pi^2T^3}\nu_F V \int\limits_0^{\Delta(T)} \Delta^3 d\Delta \tag{5.56}$$

and then use the approximate result (5.38) for the temperature dependence of $\Delta(T)$. In this way we obtain finally

$$\Phi_s - \Phi_n = -V\frac{2\pi^2\nu_F}{7\zeta(3)}T_c\left(1-\frac{T}{T_c}\right)^2. \tag{5.57}$$

The difference of entropies in therefore

$$S_s - S_n = -V\frac{4\pi^2\nu_F}{7\zeta(3)}T_c\left(1-\frac{T}{T_c}\right), \tag{5.58}$$

and we recover the discontinuity (5.50) between the heat capacities as derived earlier.

Exercise 5.8

Taking into account higher order terms, calculate

$$\frac{C_s(T)}{C_n(T_c)} = 2.43 + 3.77\left(\frac{T}{T_c}-1\right). \tag{5.59}$$

It must be remarked, that in addition to the Fermi-type excitation spectrum dealt with here, the heat capacity also contains a contribution from the phonon branch. The heat capacity due to phonons is $\sim T^3$ with a small coefficient, but as $T \to 0$ it must ultimately predominate over the exponentially decreasing heat capacity (5.47).

5.4 Ginzburg-Landau Expansion

As we have seen above, the complete expression for the thermodynamic potential for a BSC superconductor cannot be treated analytically. However, in the temperature range near the transition temperature T_c we may apply the general ideas of the Ginzburg-Landau (GL) theory; see section 3.5. The startingpoint is the expression

$$\frac{1}{\beta V}(\Phi_s - \Phi_n) = \alpha_2\Delta^2 + \alpha_4\Delta^4, \tag{5.60}$$

which may be viewed as a Taylor expansion of the thermodynamic potential with respect to Δ in which only the first two terms have been retained. These terms should be adequate so long as one stays near the second-order phase transition.

We have already discussed in section 3.5 that two cases may arise depending on whether the coefficient α_2 is positive or negative. If it is positive, the minimum occurs at $\bar{\Delta} = 0$ corresponding to the normal state. On the other hand, if $\alpha_2 < 0$ the minimum occurs when $\bar{\Delta}^2 = -\alpha_2/2\alpha_4$. The coefficient α_2 is a function of temperature given by

$$\alpha_2 = \alpha(T - T_c). \tag{5.61}$$

Substituting these results back into (5.60), we find the difference in the thermodynamic potentials of the superconducting and normal states as

$$\frac{1}{\beta V}\left(\Phi_s - \Phi_n\right) = -\frac{\alpha^2}{2\alpha_4}\left(T_c - T\right)^2. \tag{5.62}$$

Comparison of this last expression, and the one for $\bar{\Delta}$, with the same quantities in the BCS theory (5.57) and (5.38), respectively, gives the values

$$\alpha_2 = -\frac{1}{2}\nu_F\left(1 - \frac{T}{T_c}\right), \quad \alpha_4 = \frac{7\zeta\left(3\right)}{32\pi^2}\frac{\nu_F}{T_c^2}. \tag{5.63}$$

With these identifications there is complete agreement with the relevant results obtained in the preceding section.

Exercise 5.9

a. Verify that the discontinuity (5.50) in the heat capacity is correctly given by the GL-theory.

b. Rewrite the GL-expansion for the BCS model in the form

$$\Phi_s - \Phi_n = \beta\int d^3x\left(a\eta^2 + \frac{1}{2}b\eta^4\right), \tag{5.64}$$

where

$$a = -\frac{1}{2m\xi_0^2}\left(1 - \frac{T}{T_c}\right), \tag{5.65}$$

$$b = \frac{1}{mn\xi_0^2}, \tag{5.66}$$

in terms of the BCS coherence length given by

$$\zeta_0^2 = \frac{7\xi\left(3\right)}{48\pi^2}\frac{\nu_F^2}{T_c^2}. \tag{5.67}$$

and the density $n = p_F^3/3\pi^2$. Infer the definition of the order parameter η in terms of the gap parameter.

So far we have confined ourselves to an energy gap which is constant in space. However, there are many interesting situations in which a spatial inhomogeneity is an essential feature. Such situations may also be dealt with in the framework of the GL-theory by expanding the thermodynamic potential of spatially inhomogeneous superconductors in powers of $|\eta(\mathbf{x})|^2$ and $|\nabla\eta(\mathbf{x})|^2$. To conform to the standard conventions we employ the wave function $\eta(\mathbf{x})$ as order parameter field. The latter differs by a trivial normalization factor from the gap function $\Delta(\mathbf{x})$; see exc. 5.9. The basic postulate is that, if $\eta(\mathbf{x})$ is small and varies slowly in space, the thermodynamic potential can be expanded in the form

$$\Phi_s - \Phi_n = \beta \int d^3x \left(\frac{1}{2m^*} |\nabla\eta|^2 + a\,|\eta|^2 + \frac{1}{2} b\,|\eta|^4 \right), \tag{5.68}$$

where m^* is a mass parameter. In the phenomenological theory this parameter is experimentally inaccessible, since a redefinition of m^* can always be absorbed into the normalization of the order-parameter. It is conventional to equate m^* with the electron mass m.

The form of the expansion (5.68) is established by the general consideration that the thermodynamic potential should be invariant under a global change of phase of the order-parameter. By imposing the stronger condition of local gauge invariance we introduce the coupling with the electromagnetic field through the minimal substitution $\nabla \to \nabla - 2ie\mathbf{A}$. When certain boundary conditions are imposed, the order-parameter field $\eta(\mathbf{x})$ adjusts itself so as to minimize the volume integral (5.68). The complex quantity $\eta(\mathbf{x})$ is a set of two real quantities, so that η and η^* must be regarded as independent functions in the variation. The variational problem leads to the GL-equation for the order-parameter

$$\left(-\frac{1}{2m}\nabla^2 + a + b\,|\eta|^2 \right) \eta = 0. \tag{5.69}$$

Apart from the non-linear term, the equation has the form of the Schrödinger equation with energy eigenvalue $-a$. The non linear term acts like a repulsive potential of η on itself, tending to favour order parameters which are spread out as uniformly as possible in space.

Exercise 5.10

a. Derive the GL-equation in the presence of a field $\mathbf{B} = \nabla \wedge \mathbf{A}$.

b. Varying the GL-functional with respect to $\mathbf{A}$, derive the inhomogeneous Maxwell equation (4.64) with the current density as given in (4.60).

It is immediately obvious that the GL-equation (5.69) contains a characteristic correlation length given by

$$\xi^2(T) = \frac{1}{2m\,|a|} = \xi_0^2 \left(1 - \frac{T}{T_c} \right)^{-1}, \tag{5.70}$$

where ξ_0 is the BCS coherence length given in (5.67). This defines a scale for the variations of the order-parameter. The physical significance becomes evident when we consider the

Green-function equation associated with the GL-equation (5.69) linearized around the solution $\bar{\eta} = -a/b$:

$$\left(-\nabla^2 + \xi^2\right) G_0\left(\mathbf{x}, \mathbf{x}'\right) = \delta\left(\mathbf{x} - \mathbf{x}'\right). \tag{5.71}$$

The asymptotic solution has the form

$$G_0\left(\mathbf{x}, \mathbf{x}'\right) \sim \frac{1}{4\pi\left|r\right|} e^{-r}, \tag{5.72}$$

where $r = |\mathbf{x} - \mathbf{x}'|$, as is easily checked by direct substitution. This shows that a small disturbance decays exponentially with characteristic length $\xi(T)$. This length should be large in comparison with ξ_0, i.e. the dimension of the Cooper pair, in order that all quantities vary sufficiently slowly in space. At the critical temperature the correlation length $\xi(T)$ diverges as $|T_c - T|^{-\nu}$, with $\nu = \frac{1}{2}$ the mean field value for the critical exponent ν. Hence, the condition is in general satisfied near the transition point.

The GL-expansion is valid near the critical temperature, but not too close because of the occurrence of critical fluctuations. This anomalous increase in the fluctuations of the order-parameter is due to the flatness of the thermodynamic potential minimum near the transition point. We may estimate the range of this so-called Ginzburg region by writing the GL-functional in terms of dimensionless fields. We rescale $\mathbf{x} = \xi(T)\mathbf{y}$ and $\beta\xi^3|a||\eta|^2 = |\chi|^2$. Then we may write

$$\Phi_s - \Phi_n = \int d^3y \chi^* \left(\nabla_y^2 + 1 - g\left|\chi\right|^2\right)\chi, \tag{5.73}$$

where the dimensionless coupling constant, which can be calculated with the help of (5.65) and (5.66), appears as

$$g^{-1}\alpha\left(\frac{T_F}{T_c}\right)^2\left(1 - \frac{T}{T_c}\right)^{\frac{1}{2}}, \tag{5.74}$$

in terms of the critical temperature and the Fermi temperature $T_F = p_F^2/2m$. The numerical proportionality constant is of order one. We expect the theory to break down if $g > 1$. In the present case this condition is extremely weak since it implies the Ginzburg criterium

$$1 - \frac{T}{T_c} > \left(\frac{T_c}{T_F}\right)^4. \tag{5.75}$$

The ration $T_c/T_f \sim 10^{-3} - 10^{-4}$ is very small. Hence, this condition is satisfied almost up to the transition point itself and the fluctuation region for the transition practically disappears. This explains of course why the GL-theory as been so successful in describing the superconductivity.

From the derivation of (5.73) it is obvious that the critical exponent of the coupling constant g depends on the dimensionality of space. In fact, in D dimensions one finds

$$g \quad \propto \quad \left|T - T_c\right|^{(D-4)/2}. \tag{5.76}$$

This critical exponent is such that for $D > 4$, $g \to 0$ as $T \to T_c$, implying that a perturbative expansion becomes increasingly accurate as one approaches the critical point.

On the other hand, for $D < 4$, $g \to \infty$ as $T \to T_c$ and perturbation theory breaks down close to the transition temperature. In this Ginzburg region the GL-theory is invalid.

Exercise 5.11

a. Write $\Delta(\mathbf{x}) = e^{i\phi(\mathbf{x})}[|\bar{\Delta}| + f(\mathbf{x})]$ and derive the linearized GL-equations satisfied by the two real fields $\phi(\mathbf{x})$ and $f(\mathbf{x})$.

b. Argue that $f(\mathbf{x})$ may be regarded as a massive mode with mass squared $m_f^2 = 2\zeta^{-1}(T)$, and that the Goldstone mode $\phi(\mathbf{x})$ may be regarded as massless.

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