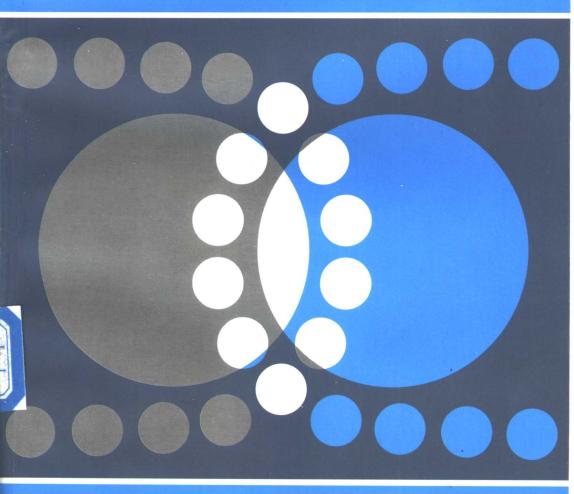
Statistical Physics

Part 2

Course of Theoretical Physics Volume 9

E. M. Lifshitz and L. P. Pitaevskii

统计物理学 第2分册



STATISTICAL PHYSICS

Part 2
Theory of the Condensed State

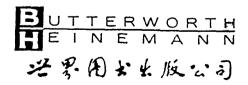
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PREFACE

As a brief characterization of its content, this ninth volume in the Course of Theoretical Physics may be said to deal with the quantum theory of the condensed state of matter. It opens with a detailed exposition of the theory of Bose and Fermi quantum liquids. This theory, set up by L. D. Landau following the experimental discoveries by P. L. Kapitza, is now an independent branch of theoretical physics. Its importance is in fact measured not so much by even the remarkable phenomena that occur in the liquid isotopes of helium as by the fact that the concepts of a quantum liquid and its spectrum are essentially the foundation for the quantum description of macroscopic bodies.

For example, a thorough understanding of the properties of metals involves treating the electrons in them as a Fermi liquid. The properties of the electron liquid are, however, complicated by the presence of the crystal lattice, and a study of the simpler case of a homogeneous isotropic liquid is a necessary preliminary step in the construction of the theory. Similarly, superconductivity in metals, which may be regarded as superfluidity of the electron liquid, is difficult to understand clearly without a previous knowledge of the simpler theory of superfluidity in a Bose liquid.

The Green's function approach is an indispensable part of the mathematical formalism of modern statistical physics. This is not only because of the convenience of calculation of Green's functions by the diagram technique, but particularly because the Green's functions directly determine the spectrum of elementary excitations in the body, and therefore constitute the language that affords the most natural description of the properties of these excitations. In the present volume, therefore, considerable attention is paid to methodological problems in the theory of Green's functions of macroscopic bodies. Although the basic ideas of the method are the same for all systems, the specific form of the diagram technique is different in different cases. It is consequently natural to develop these methods for the isotropic quantum liquids, where the essence of the procedure is seen in its purest form, without the complications arising from spatial inhomogeneity, the presence of more than one kind of particle, and so on.

For similar reasons, the microscopic theory of superconductivity is described with the simple model of an isotropic Fermi gas with weak interaction, disregarding the complications due to the presence of the crystal lattice and the Coulomb interaction.

In respect of the chapters dealing with electrons in the crystal lattice and

with the theory of magnetism, we must again stress that this book is part of a course of theoretical physics and in no way attempts to be a textbook of solid state theory. Accordingly, only the most general topics are discussed here, and no reference is made to problems that involve the use of specific experimental results, nor to methods of calculation that have no evident theoretical basis. Moreover, this volume does not include the transport properties of solids, with which we intend to deal in the next and final volume of the *Course*.

Finally, this book also discusses the theory of electromagnetic fluctuations in material media and the theory of hydrodynamic fluctuations. The former was previously included in Volume 8, *Electrodynamics of Continuous Media*. Its transfer to the present volume is a consequence of the need to make use of Green's functions, whereby the entire theory can be simplified and made more convenient for application. It is also more reasonable to treat electromagnetic and hydrodynamic fluctuations in the same volume.

This is Volume 9 of the Course of Theoretical Physics (Part 1 of Statistical Physics being Volume 5). The logic of the arrangement is that the topics dealt with here are closely akin also to those in fluid mechanics (Volume 6) and macroscopic electrodynamics (Volume 8).

L. D. Landau is not among those who have actually written this book. But the reader will quickly observe how often his name occurs in it: a considerable part of the results given here are due to him, alone or with his pupils and colleagues. Our many years' association with him enables us to hope that we have accurately reflected his views on these subjects—while at the same time, of course, having regard to developments in the fifteen years since his work was so tragically terminated.

We should like to express here our thanks to A. F. Andreev, I. E. Dzyaloshinskii and I. M. Lifshitz for many discussions of topics in this book. We have had great benefit from the well-known book *Quantum Field Theoretical Methods in Statistical Physics* (Pergamon, Oxford, 1965) by A. A. Abrikosov, L. P. Gor'kov and I. E. Dzyaloshinskii, one of the first books in the literature of physics to deal with the new methods of statistical physics. Lastly, we are grateful to L. P. Gor'kov and Yu. L. Klimontovich for reading the book in manuscript and making a number of comments.

April 1977

E. M. LIFSHITZ L. P. PITAEVSKII

NOTATION

VECTOR suffixes are denoted by Latin letters i, k, \ldots Spin indices are denoted by Greek letters α, β, \ldots Summation is implied over all repeated indices.

"4-vectors" (see the footnote to equation (13.8)) are denoted by capital letters X, P, \ldots

Volume element dV or d^3x .

Limit on tending to zero from above or below +0 or -0.

Operators are denoted by a circumflex.

Hamiltonian \hat{H} , $\hat{H}' = \hat{H} - \mu \hat{N}$.

Perturbation operator \hat{V} .

 ψ operators in the Schrödinger representation $\hat{\psi}$, $\hat{\psi}^+$; in the Heisenberg representation $\hat{\Psi}$, $\hat{\Psi}^+$; in the Matsubara representation $\hat{\Psi}^M$, $\hat{\Psi}^M$.

Green's functions G, D.

Temperature Green's functions \mathcal{Q}, \mathcal{D} .

Thermodynamic quantities are denoted as in Part 1, for example T temperature, V volume, P pressure, μ chemical potential.

Magnetic field H; magnetic induction B; external magnetic field S.

References to earlier volumes in the Course of Theoretical Physics:

Mechanics = Vol. 1 (Mechanics, third English edition, 1976).

Fields = Vol. 2 (The Classical Theory of Fields, fourth English edition, 1975).

QM = Vol. 3 (Quantum Mechanics, third English edition, 1977).

QE = Vol. 4 (Quantum Electrodynamics, second English edition, 1982).

Part 1 = Vol. 5 (Statistical Physics, Part 1, third English edition, 1980).

FM = Vol. 6 (Fluid Mechanics, first English edition, 1959).

ECM = Vol. 8 (Electrodynamics of Continuous Media, second English edition, 1984).

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CHAPTER I

THE NORMAL FERMI LIQUID

§ 1. Elementary excitations in a quantum Fermi liquid

At temperatures so low that the de Broglie wavelength corresponding to the thermal motion of the atoms in a liquid becomes comparable with the distances between the atoms, the macroscopic properties of the liquid are determined by quantum effects. The theory of such quantum liquids is of considerable fundamental interest, although there exist in Nature only two such that are literally liquids, the liquid isotopes of helium He³ and He⁴ at temperatures $\sim 1\text{--}2^\circ\text{K}$. All other substances solidify well before quantum effects become important in them. In this connection, it may be recalled that according to classical mechanics all bodies should be solid at absolute zero (see Part 1, §64). Helium, however, because of the peculiarly weak interaction between its atoms, remains liquid down to temperatures where quantum phenomena come into effect, whereupon it need not solidify.

The calculation of the thermodynamic quantities for a macroscopic body requires a knowledge of its energy level spectrum. In a system of strongly interacting particles such as a quantum liquid, we can refer, of course, only to levels that correspond to quantum-mechanical stationary states of the whole liquid, not to states of the individual atoms. In calculating the partition function at sufficiently low temperatures, we are to take account only of the weakly excited energy levels of the liquid, lying fairly close to the ground state.

The following point is of fundamental importance for the whole theory. Any weakly excited state of a macroscopic body may be regarded, in quantum mechanics, as an assembly of separate elementary excitations. These behave like quasi-particles moving in the volume occupied by the body and possessing definite energies ε and momenta \mathbf{p} . The form of the function $\varepsilon(\mathbf{p})$, the dispersion relation for the elementary excitations, is an important characteristic of the energy spectrum of the body. It must again be emphasized that the concept of elementary excitations arises as a means of quantum-mechanical description of the collective motion of the atoms in a body, and the quasiparticles cannot be identified with the individual atoms or molecules.

There are various types of energy spectrum that can in principle occur in quantum liquids. There will be completely different macroscopic properties also, depending on the type of spectrum. We shall begin by considering a liquid

1

with what may be called a *Fermi* spectrum. The theory of such a Fermi liquid is due to L. D. Landau (1956-1958); he derived the results given in §§1-4.

The energy spectrum of a Fermi quantum liquid has a structure which is to some extent similar to that of an ideal Fermi gas (of particles with spin $\frac{1}{2}$). The ground state of the latter corresponds to the occupation by particles of all the states within the *Fermi sphere*, a sphere in momentum space whose radius p_F is related to the gas density N/V (number of particles per unit volume) by

$$N/V = 2 \cdot 4\pi p_F^3 / 3(2\pi\hbar)^3$$

= $p_F^3 / 3\pi^2\hbar^3$; (1.1)

see Part 1, §57. The excited states of the gas occur when the particles pass from states of the occupied sphere to some states with $p > p_F$.

In a liquid, of course, there are no quantum states for individual particles, but to construct the spectrum of a Fermi liquid we start from the assumption that the classification of energy levels remains unchanged when the interaction between the atoms is gradually "switched on", i.e. as we go from the gas to the liquid. In this classification the role of the gas particles is taken by the elementary excitations (quasi-particles), whose number is equal to the number of atoms and which obey Fermi statistics.

It is evident that such a spectrum can occur only for a liquid of particles with half-integral spin: the state of a system of bosons (particles with integral spin) cannot be described in terms of quasi-particles obeying Fermi statistics. At the same time it must be emphasized that a spectrum of this type cannot be a universal property of all such liquids. The type of spectrum depends also on the specific nature of the interaction between atoms. This is clear from the following simple consideration: if the interaction is such that it causes the atoms to tend to associate in pairs, then in the limit we obtain a molecular liquid consisting of particles (molecules) with integral spin, for which the spectrum under consideration is certainly impossible.

Each of the quasi-particles has a definite momentum \mathbf{p} (we shall return later to the question of the validity of this assertion). Let $n(\mathbf{p})$ be the momentum distribution function of the quasi-particles, normalized by the condition

$$\int n \, d\tau = N/V, \quad d\tau = d^3p/(2\pi\hbar)^3;$$

this condition will later be made more precise. The classification principle mentioned above consists in supposing that, if this function is specified, the energy E of the liquid is uniquely determined and that the ground state corresponds to a distribution function in which all states are occupied within the Fermi sphere, whose radius p_F is related to the density of the liquid by the same formula (1.1) as for an ideal gas.

[†] To anticipate, we may mention here for the avoidance of misunderstanding that we are referring to a non-superfluid (normal) Fermi liquid, such as is the liquid isotope He³, with the reservation made in the third footnote to §54.

It is important to emphasize that the total energy E of the liquid is not simply the sum of the energies ε of the quasi-particles. In other words, E is a functional of the distribution function that does not reduce to the integral $\int n\varepsilon \, d\tau$ (as it does for an ideal gas, where the quasi-particles are the same as the actual particles and do not interact). Since the primary concept is E, the question arises how the energy of the quasi-particles is to be defined, with allowance for their interaction.

For this purpose, let us consider the change of E due to an infinitesimal change in the distribution function. It can manifestly be defined as the integral of an expression linear in the variation δn , i.e. it has the form

$$\delta E/V = \int \varepsilon(p) \delta n \, d\tau.$$

The quantity ε is the functional derivative of the energy E with respect to the distribution function. It corresponds to the change in the energy of the system when a single quasi-particle with momentum \mathbf{p} is added. This quantity plays the role of the Hamiltonian function of a quasi-particle in the field of the other particles. It is also a functional of the distribution function, i.e. the form of the function $\varepsilon(\mathbf{p})$ depends on the distribution of all the particles in the liquid.

In this connection it may be noted that an elementary excitation in the type of spectrum considered may in a certain sense be treated like an atom in the self-consistent field of the other atoms. This self-consistency is, of course, not to be understood in the sense usual in quantum mechanics. Here its nature is more profound; in the Hamiltonian of the atom, not only is allowance made for the effect of the surrounding particles on the potential energy, but the dependence of the kinetic-energy operator on the momentum operator is also modified.

Hitherto we have ignored the possible spin of the quasi-particles. Since spin is a quantum-mechanical quantity, it cannot be treated classically, and we must therefore regard the distribution function as a statistical matrix with respect to the spin. The energy ε of an elementary excitation is in general not only a function of the momentum but also an operator with respect to the spin variables, which may be expressed in terms of the quasi-particle spin operator \hat{s} . In a homogeneous isotropic liquid (not in a magnetic field and not ferromagnetic) the operator \hat{s} can appear in the scalar function ε only in the form of the scalars \hat{s}^2 and $(\hat{s}.p)^2$; the first power of the product $\hat{s}.p$ is inadmissible, since the spin vector is an axial vector and this product is therefore a pseudoscalar. The square $\hat{s}^2 = s(s+1)$, and for spin $s = \frac{1}{2}$ the scalar $(\hat{s}.p)^2 = \frac{1}{4}p^2$ also reduces to a constant independent of \hat{s} . Thus in this case the energy of a quasi-particle is independent of the spin operator, and all the energy levels of the quasi-particles are doubly degenerate.

The statement that a quasi-particle has spin essentially expresses the fact that this degeneracy exists. In this sense we can say that the spin of the quasi-particles in a spectrum of the type considered is always $\frac{1}{2}$, whatever the spin of the actual particles in the liquid. For with any spin s other than $\frac{1}{2}$ the terms

of the form $(\hat{s}.\mathbf{p})^2$ would give a splitting of the (2s+1)-fold degenerate levels into $\frac{1}{2}(2s+1)$ doubly degenerate levels. In other words, $\frac{1}{2}(2s+1)$ different branches of the function $\varepsilon(\mathbf{p})$ would appear, each corresponding to "quasiparticles with spin $\frac{1}{2}$ ".

As already mentioned, when the spin of the quasi-particles is taken into account the distribution function becomes a matrix or an operator $\hat{n}(\mathbf{p})$ with respect to the spin variables. This operator may be explicitly written as an Hermitian statistical matrix $n_{\alpha\beta}(\mathbf{p})$, where α and β are spin matrix indices taking the two values $\pm \frac{1}{2}$. The diagonal matrix elements determine the numbers of quasi-particles in particular spin states. The normalization condition for the quasi-particle distribution function must therefore now be written

$$\operatorname{tr} \int \hat{n} \, d\tau \equiv \int n_{xx} \, d\tau = N/V, \quad d\tau = d^3p/(2\pi\hbar)^3, \tag{1.2}$$

where tr denotes the trace of the matrix with respect to the spin indices.

The quasi-particle energy $\hat{\epsilon}$ is in general also an operator (a matrix with respect to the spin variables). It must be defined by

$$\delta E/V = \operatorname{tr} \int \hat{\varepsilon} \, \delta \hat{n} \, d\tau \equiv \int \varepsilon_{\alpha\beta} \, \delta n_{\beta\alpha} \, d\tau. \tag{1.3}$$

If there is no spin dependence of the distribution function and the energy, so that $n_{\alpha\beta}$ and $\varepsilon_{\alpha\beta}$ reduce to unit matrices:

$$n_{\alpha\beta} = n\delta_{\alpha\beta}, \quad \varepsilon_{\alpha\beta} = \varepsilon\delta_{\alpha\beta},$$
 (1.4)

then the taking of the trace in (1.2) and (1.3) amounts to simply multiplying by 2:

$$2 \int n \, d\tau = N/V, \quad \delta E/V = 2 \int \varepsilon \, \delta n \, d\tau. \tag{1.5}$$

It is easy to see that in statistical equilibrium the quasi-particle distribution function is an ordinary Fermi distribution, the energy being represented by the quantity $\hat{\epsilon}$ defined in (1.3). For, because the energy levels of the liquid and of the ideal Fermi gas are classified in the same manner, the entropy S of the liquid is determined by a similar combinatorial expression

$$S/V = -\text{tr} \int \{ \hat{n} \log \hat{n} + (1 - \hat{n}) \log (1 - \hat{n}) \} d\tau$$
 (1.6)

to that for a gas (Part 1, §55). Varying this expression with the additional conditions of constant total number of particles and constant total energy,

$$\delta N/V = \operatorname{tr} \int \delta \hat{n} \, d\tau = 0, \quad \delta E/V = \operatorname{tr} \int \hat{\epsilon} \, \delta \hat{n} \, d\tau = 0,$$

we obtain the required distribution:

$$\hat{n} = [e^{(\hat{\epsilon}^{-\mu})/T} + 1]^{-1}, \tag{1.7}$$

where μ is the chemical potential of the liquid.

[†] Here and throughout, summation is as usual implied over repeated indices.

When the quasi-particle energy is independent of the spin, formula (1.7) signifies a similar relation between n and ε :

$$n = [e^{(e^{-\mu})T} + 1]^{-1}. \tag{1.8}$$

At T=0, the chemical potential is equal to the limiting energy on the surface of the Fermi sphere:

$$[\mu]_{T=0} = \varepsilon_F \equiv \varepsilon(p_F).$$
 (1.9)

It must be emphasized that, despite the formal analogy between the expression (1.8) and the ordinary Fermi distribution, it is not identical with the latter: since ε itself is a functional of n, formula (1.8) is strictly speaking a complicated implicit expression for n.

Let us now return to the assumption that a definite momentum can be assigned to each quasi-particle. The condition for this assumption to be valid is that the uncertainty in the momentum (due to the finite mean free path of the quasi-particle) should be small not only in comparison with the momentum itself but also in comparison with the width Δp of the "transitional zone" of the distribution, over which it differs appreciably from a step function:

$$\theta(\mathbf{p}) \equiv \theta(p) = 1 \quad \text{for} \quad p < p_F, \\ = 0 \quad \text{for} \quad p > p_F.$$
 (1.10)

It is easy to see that this condition is satisfied if the distribution n(p) differs from (1.10) only in a small region near the surface of the Fermi sphere. For, by the Pauli principle, only quasi-particles in the transitional zone of the distribution can undergo mutual scattering, and as a result of this scattering they must enter free states in that zone. Hence the collision probability is proportional to the square of the width of the zone. Accordingly, the uncertainty in the energy and hence that in the momentum of the quasi-particle are both proportional to $(1p)^2$. It is therefore clear that, when Δp is sufficiently small, the uncertainty in the momentum will be small only not in comparison with p_F but also with Δp .

Thus the method described is valid only for excited states of the liquid which are described by a quasi-particle distribution function differing from a step function in just a narrow region near the Fermi surface. In particular, for thermodynamic equilibrium distributions only sufficiently low temperatures are permissible. The (energy) width of the transitional zone of the equilibrium distribution is of the order of T. The quantum uncertainty in the energy of a quasi-particle, due to collisions, is of the order of \hbar/τ , where τ is the mean free time of the quasi-particle. The condition for the theory to be applicable is therefore

$$\hbar/\tau \ll T. \tag{1.11}$$

For future reference, it may be noted that the derivative $\theta'(p) = -\delta(p - p_p)$, since both sides give unity on integration over any range of p that includes the point $p = p_p$.

According to the preceding discussion, the time τ is inversely proportional to the squared width of the transitional zone:

$$\tau \propto T^{-2}$$
.

so that (1.11) is certainly satisfied as $T \to 0$. For a liquid in which the interaction between particles is not weak, all the energy parameters are of the same order as the limiting energy ε_F ; in this sense, the condition (1.11) is equivalent to $T \ll |\varepsilon_F|^{\frac{1}{\tau}}$

For almost step-function distributions (i.e. those close to the distribution for T=0), as a first approximation we can replace the functional ε by its value calculated with $n(\mathbf{p})=\theta(\mathbf{p})$. Then ε becomes a definite function of the magnitude of the momentum, and (1.7) becomes the ordinary Fermi distribution.

Near the surface of the Fermi sphere, where alone the function $\epsilon(\mathbf{p})$ has a direct physical significance, it can then be expanded in powers of the difference $p - p_F$. We have

$$\varepsilon - \varepsilon_F \approx v_F(p - p_F),$$
 (1.12)

where

$$\mathbf{v}_{\mathbf{F}} = [\partial \varepsilon / \partial \mathbf{p}]_{\mathbf{p} = p_{\mathbf{F}}} \tag{1.13}$$

is the "velocity" of the quasi-particles on the Fermi surface. In an ideal Fermi gas, where the quasi-particles are identical with the actual particles, we have $\varepsilon = p^2/2m$, and so $v_F = p_F/m$. By analogy we can define for a Fermi liquid the quantity

$$m^* = p_F/v_F,$$
 (1.14)

called the effective mass of the quasi-particle; it is positive (see the end of §2).

In terms of the quantities thus defined, the condition for the theory to be applicable may be written $T \ll v_F p_F$, and only quasi-particles with momenta p such that $|p-p_F| \ll p_F$ have any real meaning. This important fact, in particular, makes the relation (1.1) between p_F and the density of the liquid non-trivial, since its intuitive derivation (for a Fermi gas) is based on the concept of particles in states occupying the whole Fermi sphere, not just the neighbourhood of its surface.

The effective mass determines, in particular, the entropy S and the specific heat C of the liquid at low temperatures. These are given by the same formula as for an ideal gas (Part 1, §58), in which we need only replace the particle mass m by the effective mass m^* :

$$S = C = V\gamma T$$
, $\gamma = m^* p_F/3\hbar^3 = (\frac{1}{3}\pi)^{2/3} (m^*/\hbar^2) (N/V)^{1/3}$; (1.15)

* The proof of (1.1) involves the use of more complicated mathematical methods, and is given in \$20 below.

[†] For liquid He³, however, the range of quantitative applicability of the theory is shown by experiment to be in fact limited to $T \lesssim 0.1$ °K (whereas $|\varepsilon_F| \approx 2.5$ °K).

because of the linear dependence on T, S and C are the same. This follows because the expression (1.6) for the entropy in terms of the distribution function is the same for a liquid and for a gas, and in the calculation of this integral only the range of momenta near p_F is important, in which the quasi-particle distribution function in the liquid and the particle distribution function in the gas are given by the same expression (1.8).

Before the theory is further developed, the following remark should be made. Although this method of defining the quasi-particles in a Fermi liquid by exact analogy with the particles in a gas is the most convenient in systematically deriving the theory, the corresponding physical picture has the disadvantage of involving the unobservable filled Fermi sphere of quasi-particles. This could be eliminated by a formulation in which the elementary excitations occur only when $T \neq 0$. In such a picture, the elementary excitations are represented by quasi-particles outside the Fermi sphere and "holes" within it; the former are to be assigned, in the approximation corresponding to (1.12), the energy $\varepsilon = v_F(p-p_F)$, and the latter the energy $\varepsilon = v_F(p_F-p)$. The statistical distribution of each is given by the Fermi distribution formula with zero chemical potential (in accordance with the fact that the number of elementary excitations is here not constant, but is itself determined by the temperature):

$$n = [e^{\varepsilon/T} + 1]^{-1}. (1.16)$$

The elementary excitations in this picture appear or disappear only in pairs, and so the total numbers of excitations with $p > p_F$ and $p < p_F$ are always the same.

With this definition of the elementary excitations, their energy is certainly positive, being the excess of the energy of the excited level over that of the ground level of the system. The energy of the quasi-particles defined by (1.3) may be either positive or negative.

Moreover, for a liquid at zero temperature and zero pressure, the quantity $\varepsilon_F = \mu$ is certainly negative, and the values of ε close to ε_F are therefore negative also. This is clear, since, when T=0 and P=0, $-\mu$ is a positive quantity, the limiting value of the heat of evaporation of the liquid per particle.

[†] For liquid He³ at zero pressure, $p_F/\hbar = 0.8 \times 10^8 \, \mathrm{cm}^{-1}$; $m^* = 3.1 \, m$ (He³); p_F is found from the density of the liquid, and m^* from its specific heat.

It will be recalled (cf. Part 1, §63) that under such conditions the number of quasi-particles N_{ep} is determined by the condition for thermodynamic equilibrium: the free energy F is a minimum as a function of N_{ep} for given temperature and volume: $(\partial F/\partial N_{ep})_{T, F} = 0$. This derivative is, however, just the "chemical potential of the quasi-particles"; it should not be confused with the chemical potential μ of the liquid, which is determined by the derivative of F with respect to the number of actual particles N.