Zeitschrift: Helvetica Physica Acta
Band: 65 (1992)
Heft: 2-3

Artikel: Theories of superconductivity (a few remarks)
Autor: Ginzburg, V.L.
DOI: https://doi.org/10.5169/seals-116395

Helv Phys Acta
Vol. 65 (1992)

0018-0238/92/030173-72$1.50+0.20/0

Theories of superconductivity (a few remarks)[1]

By V. L. Ginzburg

P. N. Lebedev Physical Institute, USSR Academy of Sciences, Leninsky Prospect 53, 117924, Moscow, USSR

Abstract. The early history in the development of superconductivity. Idea of pairing, Schafroth and BCS types of theories. Some remarks on present state of the microscopical theory of high-temperature superconductors (HTSC). Mean field macroscopic theory of superconductivity and its specific features in HTSC. About generalized macroscopic theory applicable in critical region. Concluding remarks.

1. Introduction. Early attempts to create the theory of superconductivity

I am making this report by the offer of the Organizing Committee of the Conference. This fact allows me to worry less of whether such a communication is appropriate here. Since "theory of superconductivity" is a too extensive topic, it is only possible to make here some remarks both of historical character and associated with high-temperature superconductivity (HTSC).

Superconductivity was discovered in 1911, exactly 80 years ago. It was not a sensation like the one caused by the discovery of HTSC in 1987. In particular, Kamerling Onnes was awarded the Nobel prize in 1913 for his investigations on the properties of matter at low temperatures which led, inter alia, to the production of liquid helium. Superconductivity was not mentioned at all, although in his Nobel speech Onnes touched upon this question, as well. The time was, of course, quite different, there were not many physicists, and the range of investigations was different, too (suffice it to say that for a period of 15 years—since 1908 to 1923—liquid helium had been produced only in Leiden). But an essential fact was that the discovery of superconductivity (or, more precisely, the discovery of a very strong and sharp decrease in resistance) did not come into contradiction with anything known before. Moreover, even before that it had been hypothesized as one of the possibilities that at a certain temperature (not necessarily at $T \to 0$) metal resistance may be equal to zero. As a matter of fact, it was impossible to calculate the temperature dependence of resistance $R(T)$ not only in 1911, but up to the late

[1] The paper prepared for the International Conference on Physics in Two Dimensions, Neuchatel, Switzerland, August 19–23, 1991

[2] Not to overload the text, I shall try to quote only the review papers containing references to original literature. So, as far as the history of the development of the theory of metals is concerned, I refer to the review [1]

twenties because the theory of metals (even in the normal state) was absent. In Drude's theory (1900)[2], however, the concept of electron gas in metals was introduced and a number of important relations derived. But the model was absolutely contradictory since the classical electron gas should have made a large contribution to the specific heat, which contradicted experiment.

As is well known, the situation changed radically only after the creation of quantum mechanics and the application of Fermi-Dirac statistics to the electron gas. Within several years (beginning from 1926–27) Pauli, Sommerfeld, Bethe, Bloch, Peierls and other scientists created the basic principles of modern quantum theory of metals in the normal state [1, 2]. It was just at that time that it became clear that superconductivity is actually a remarkable phenomenon, absolutely unclear in the framework of the model of electron gas in metals. For example, Bethe wrote in 1933 (see Ref. [2], p. 555): "The success in the theory, in the explanation of normal phenomena in conductivity is great, whereas very little has as yet been done in solving the problem of superconductivity. Only a number of hypotheses exist which until now have in no way been worked out and whose validity cannot therefore be verified". Which hypotheses are meant here is clear from Refs. [1, 2], and all of them appeared to be invalid. The most remarkable physicists, including Einstein and Bohr [1], tried to have insight into the mechanism of superconductivity. It was undoubted that the one-electron model of metal cannot be used to describe superconductivity, but what interelectron interaction should be taken into account and, which is most important, how this should be done, remained quite unclear.

The isotope effect, that is the dependence of the critical temperature T_c on the ion mass **M** of a metal, was discovered in 1950. This fact suggested that the account of interaction between the conduction electrons and lattice oscillations or, in another language, phonons is decisive for the understanding of superconductivity. But an account of variations of the proper electron energy as a result of their interaction with phonons did not at all lead to the theory of superconductivity [3, 4, 11]. True, the first successful microtheory of superconductivity [5] formulated by Bardeen, Cooper, and Schrieffer (BCS) in 1957 (that is, a whole 46 years after the discovery of superconductivity) considers the electron-phonon interaction, but this is not the main thing. Superconductivity is a consequence of attraction among electrons situated near the Fermi surface, which leads to instability of the ordinary Fermi distribution of electrons over energy, to pair creation and to a gap in the spectrum of quasiparticles. The electron-phonon interaction can cause, and in a number cases does cause such an attraction. But obviously superconductivity can also occur for another attraction mechanism. I shall not mention here superconductivity and superfluidity of neutron stars or superfluidity in low-temperature phases of a liquid ^3He (recall that superconductivity is, in fact, the same as superfluidity, but for charged particles). Suffice it to say that the isotope effect, even for well-known superconductors, is sometimes practically absent, and in the basic formula of the BCS model for critical temperature

$$T_c = \Theta e^{-1/\lambda} \tag{1}$$

the parameter λ characterizes, quite independently of its nature, the attraction force between electrons (quasiparticles) near the Fermi surface in the energy-band width of the order of $k_B\Theta$. Sometimes λ can be written in the form $\lambda = N(0)V$, where $N(0)V$ is the state density on the Fermi surface in normal state and V is a certain mean matrix element of the interaction energy corresponding to attraction [5]. I repeat that the nature of attraction is here of no importance at all. If the attraction is associated with phonons then, naturally, the parameter Θ in (1) is of the order of the Debye temperature Θ_D.

Before returning to the microtheory of superconductivity I'd like to note that the great success of the theory of metals in normal state [2, 3] eclipsed the fact that the foundation of the theory was rather flimsy. Indeed, the kinetic energy of electrons in a metal (which is of the order of the Fermi energy E_F) is not at all high compared to their Coulomb interaction energy (e.g. for Ag, for the electron concentration $n = 5.9 \cdot 10^{22}\,\mathrm{cm}^{-3}$ the Fermi energy $E_F = 8.5 \cdot 10^{-12}$ erg and $e^2 n^{1/3} = 19.3 \cdot 10^{-12}$ erg). Landau liked to say that "nobody had abrogated the Coulomb law" and the conduction electrons in a metal obviously formed a liquid. Why then does if behave, sometimes even in a good approximation, as an ideal gas? But the winner is always right, and this question worried evidently few people at that time. The solution, as we know, was found (Landau, 1956–1958) when the theory of Fermi-liquid was formulated. In its developed form [6] this theory is not at all simpler than the modern theory of superconductivity.

2. The idea of pairing. The Schafroth and the Bardeen–Cooper–Schrieffer models

Superfluidity of liquid helium II was discovered (it is more correct to say, finally discovered, see Refs. [7, 8]) in 1938. After that it became clear that superconductivity is superfluidity of a charged electron liquid in metals [9]. It is of interest that at first Landau did not associate superfluidity of He II with Bose–Einstein condensation and generally with Bose–Einstein statistics for He atoms [9, 10]. Some other physicists, on the contrary, thought of Bose-statistics of ^{4}He as essential [7, 10] and this became obvious after liquid ^{3}He was obtained in 1948. It seemed that it was already not far from the idea of explaining superconductivity by electron pairing with a subsequent Bose–Einstein pair condensation. But it was not easy to assume pairing, for "nobody had abrogated the Coulomb law". Now we understand, of course, that electrons in a medium can attract each other (formally this follows even from the generalized Coulomb law $e^2/\Theta r$, where Θ is permittivity of the medium, which can be negative). In any case, the idea of pairing was rather daring, and to me, for example, it had not occurred explicitly, although I noticed that for a charged Bose-gas the Meissner effect [11] should be observed. As far as I know, Ogg [12] was the first to employ pairing for the explanation of superconductivity, and then this idea was developed by Schafroth [13, 14]. The Bose-gas model, with the use of formulae for the ideal Bose-gas, is meaningful if pairs are small, local. In other words, the size of pairs ξ_0 should be less or at any rate of the order of the distance between pairs, $n^{-1/3}$ (n is pair concentration). Such a model can be called the Schafroth model or the model with local pairs. For orientation the following formula for the Bose–Einstein ideal gas condensation

$$T_c = \frac{3.31\hbar^2 n^{2/3}}{m^* k_B} = 2.9 \cdot 10^{-11} \left(\frac{m}{m^*}\right)(n_{cm^{-3}})^{2/3}\ \mathrm{K} \tag{2}$$

is used as T_c. Here m^* is the mass of the pair, $m = 9.1 \cdot 10^{-28}$ g is the electron mass, and the spin of the pair is assumed to be equal to zero (for a spin 1 pair the T_c value is $g^{2/3} = 3^{2/3} = 2.08$ times less; $g = 2s + 1$, where s is the particle-pair spin). If we apply formula (2) to liquid ^{4}He, we obtain the value $T_c = 3.1$ K. At the same time the temperature of the λ-point in liquid ^{4}He is equal to $T_\lambda = 2.17$ K. From this it is clear that for orientation formula (2) can be successfully used even for a liquid. A large number of papers have been lately devoted to the Schafroth model in connection with the problem of high temperature superconductivity. For the corresponding review see Ref. [15].

The principal difference between the Schafroth and BCS models is that in the latter the pairs (Cooper pairs) exist, if we do not speak of fluctuations, only at $T < T_c$. At $T > T_c$, that is, above critical temperature, there are no pairs, and the superconducting transition is a second-order transition. Moreover, the BCS theory itself is a typical mean-field theory. In the Schafroth model, pairs "condense" (more precisely, begin to condense) at T_c, so that at $T < T_c$ the liquid (gas) is superfluid (superconducting). But quite real pairs, to say nothing of fluctuational pairs, exist also at $T > T_c$. In the case of helium, the role of such pairs is played by helium atoms themselves, and they break (stop being bosons) only at temperatures $T^* \sim 10^4 - 10^5$ K under ionization. Of course, in the case of local electron pairs (which are more often called bipolarons), the pairs break generally not at so high temperatures, say, at $T^* \sim \Theta_D$.

We have already said something about the BCS model. Note also that in the original paper by Bardeen *et al.* [5] there is no mentioning the connection between superfluidity and superconductivity, the Bose–Einstein condensation or individual pairs proper. This is, generally, clear because the size of Cooper pairs for type I superconductors, $\xi_0 \sim 10^{-5} - 10^{-4}$ cm, exceeds strongly the interatomic (and interelectron) distance $d \sim 10^{-8} - 10^{-7}$ cm. It is therefore difficult, and as a matter of fact impossible, to speak of individual pairs, and there occurs a certain unified "coherent" "collective" or "condensed" (terms do not matter) state. The simple BCS model containing in formula (1) only the parameter Θ and λ proved to be not only the first clear and definite model explaining the transition to a superconducting state[3], but was also successfully applied for the description of a number of superconductors with weak coupling $\lambda \ll 1$ (formula (1) holds only in this approximation). One of the reasons for that is isotropy (or quasi-isotropy) of some superconductors. Another reason is the application of the mean-field approximation and the conclusion concerning the second-order phase transition (see also Ref. [19]). But the macroscopic theory [16] (see item 4 below) which was in agreement

[3] In the Schafroth model [13, 14] the existence of pairs was, in fact, postulated, whereas in the BCS model [5] the ground state and many other things were considered in a consistent way.

with experiment (in Ref. [17], the BCS theory was shown to imply just the scheme [16]) was formulated on the same basis.

Sometimes it is only the model [5] that is referred to as the BCS model or theory. But the theory [5] was long ago extended to the case of intermediate and strong coupling, when $\lambda \gtrsim 1$ [18]. The corresponding theory is fairly well developed [19, 20]. Its specific feature, as in the original BCS model [5], is the second-order phase transition at $T = T_c$ and the absence, if we do not speak of fluctuations, of pairs at $T > T_c$. Such a scheme (see, in particular, Ref. [20]) is just what we shall take as the BCS theory (moreover, the attraction mechanism is not assumed to be connected with magnetic interaction or, generally, with spin effects, say, with the spin wave exchange).

3. On the microtheory in the case of high-temperature superconductors (HTSC)

The discovery of high-temperature superconductors in 1986–87 became a sensation, but not at all in theory (I have already written about this and would not like to return to it now; see Ref. [8] as well as [19, 21]). At the same time the question of the mechanisms of superconductivity in revealed HTSC materials, of course, arose. A somewhat detailed discussion of this problem and generally of the microtheory of HTSC is far beyond the scope of the present paper. And, besides, the problem on the whole is not yet clear. I'll however dare make a few remarks.

As for the cubic oxide $Ba_{1-x}K_xBiO_3$ with $T_c \lesssim 30$ K, it is a disputable question of whether it should be called a HTSC. In any case, there is obviously every reason to assume it to be a "conventional" BCS type superconductor with an electron-phonon interaction and an intermediate coupling [22]. As concerns such HTSC as cuprates, it should be noted that, first, they are anisotropic, sometimes even strongly anisotropic. Second, their T_c reaches 125 K (this is a definitely established reproducible value; it is not excluded that higher T_c values were observed but not yet reproduced). The third and the main thing is that the coherent length ξ_0 for these materials is very small as compared to conventional superconductors. For example, for $YBa_2Cu_3O_7$ the reported values are $\xi_{ab} = 14 \pm 2$ Å, $\xi_c = 1.5$–3 Å, $\delta_{ab} = 1400$ Å, $\delta_c \sim 7000$ Å (see Ref. [23]; instead of the more frequently used letter λ the penetration depth is denoted here by δ; the subscripts ab refer to the Cu_2O planes, the c-axis is perpendicular to them; finally, δ_{ab} is the Londons penetration depth for a superconducting current in the ab-plane).

So, if we speak of Cooper pairs, they are flattened "ellipsoids" and even in the ab plane are not so large as compared to the atomic size $d \sim 3$ Å. In this connection, the assumption that we are dealing with local pairs, i.e. with the Schafroth case, is even natural. Such an idea has indeed been repeatedly hypothesized [15, 24, 25]. As has already been mentioned above, real pairs in the Schafroth model exist also above T_c. No confirmation of the existence of such pairs is known to me. For this and for some other reasons partially clear from what follows, it seems to me that the Schafroth model, when applied to the known HTSC, is unlikely to be probable. The BCS model, especially with strong coupling seems, on the contrary, to be admissible. However, numerous contradictions with this model have repeatedly been reported in the literature. But according to the recent paper by Moscow authors [26] there are no such difficulties if we use consistently the Eliashberg equation and make allowance for the pair-breaking effect due to a rather high temperature. At high T_c values, when there are many real (thermal) phonons, the latter process is particularly essential. As a result, as distinct from the standard BCS theory (the theory with a weak coupling), quasiparticles ("normal" electrons and holes) exist at $T \neq 0$ not only outside the initial superconducting gap (at $T = 0$), but also inside the gap. This leads to the temperature dependence of the penetration depth of the field, which is close to that of the so-called two-liquid model (the law

$$\delta(T) = \text{const}\left[1 - \left(\frac{T}{T_c}\right)^4\right]^{-1/2};$$

see Ref. [4]). I shall emphasize that in the generalized BCS model under discussion, phonons and excitons are, in fact, equivalent in the role of bosons, whose exchange leads to electron attraction. We can only distinguish between phonons and electrons, say, in the course of neutron studies. Much is of course unclear both in experiment and in the microtheory. At the same time, the production (for example, the number of papers) is enormous, and this is a weight on my mind. I shall restrict myself here to citing the reviews devoted to the microtheory of HTSC ([15, 20, 25, 27, 28]) as well as the paper [29] elucidating the exotic anyon superconductivity.

The problem of quasi-two-dimensionality of some HTSC (which is particularly clearly pronounced in the compound $Bi_2Sr_2CaCu_2O_8$ [30]) is deserving thorough consideration. This problem is also the subject matter of a great number of papers, which are most likely to be discussed at the present Conference. I shall again restrict myself to references [31]. I permit myself to note that I have considered two-dimensional superconductivity with my colleagues in several pages [32].

4. Macroscopic theory of superconductivity

Even in the cases when there exists a perfect microtheory, a whole number of problems can and should be studied in the framework of a macrotheory. The well-known examples of combination of micro- and macrotheories is the kinetic theory of gases and hydrodynamics, as well as microscopic electrodynamics (electron theory) and macroelectrodynamics of continuous media. This also concerns, of course, the theory of superconductivity. Furthermore, the role of macrotheory of superconductivity was very important some time before, since a somewhat perfect microtheory appeared only in 1957 [5]. The main landmarks of the development of macrotheory of superconductivity are the "two-fluid" Gorter and Casimir model (1934), the Londons electrodynamics (1935) and the **Ψ**-theory of superconductivity, more often referred to as the Ginzburg–Landau theory (1950). Here, of course, I cannot dwell in detail on the corresponding constructions (see Refs. [4, 33, 34] and the literature cited there). I shall only make a few remarks.

In a superconductor there can run a superconducting current (with a density $\mathbf{j}_s$) and a normal current (with a density $\mathbf{j}_n$); the total current density is, of course, $\mathbf{j} = \mathbf{j}_s + \mathbf{j}_n$. In the local approximation corresponding to the Londons theory and to the Ψ-theory, we have $\mathbf{j}_n = \sigma_n \mathbf{E}$, where σ_n is conductivity due to "normal electrons" and $\mathbf{E}$ is the electric field strength. The gradients of the temperature ∇T and of the chemical potential are assumed to be absent. The extension to the case $\nabla T \neq 0$ allows us to consider thermoelectric phenomena [35, 36]. Below we assume for simplicity $\mathbf{j}_n = 0$ and denote the acting magnetic field by $\mathbf{H}$.

The Londons equations for $\mathbf{j}_s$ have the form

$$\operatorname{rot}(\Lambda \mathbf{j}_s) = -\frac{1}{c}\mathbf{H}, \qquad \frac{\partial(\Lambda \mathbf{j}_s)}{\partial t} = \mathbf{E}. \tag{3}$$

Together with the field equation $\operatorname{rot} \mathbf{H} = (4\pi/c)\mathbf{j}_s$ (we are considering a static or a quasistationary field), the first of the equations (3) leads to the well-known formulae (we assume $\Lambda = \text{const}$)

$$\Delta \mathbf{H} - \frac{1}{\delta^2}\mathbf{H} = 0, \qquad \Delta \mathbf{j}_s - \frac{1}{\delta^2}\mathbf{j}_s = 0, \qquad \delta^2 = \frac{\Lambda c^2}{4\pi}. \tag{4}$$

Simple model considerations permit the notation

$$\Lambda = \frac{m}{e^2 n_s}$$

and

$$\delta^2 = \frac{mc^2}{4\pi e^2 n_s},$$

when n_s is concentration of "superconducting electrons" with charge e and mass m. But the only observable quantity in this case is the penetration depth δ of the field. The extension of the scheme (3) to the anisotropic case is attained by replacement of Λ by the tensor Λ_{ik} [33, 35]. In a weak field (a field $H \ll H_c$, where H_c is the critical magnetic field) equations (3) and (4) permit solving a number of problems and are thus quite valuable. But considering destruction of superconductivity (say, of a superconducting film) in an external magnetic field or calculating the surface energy on the boundary between the superconducting and normal phases, we cannot already think of the field as weak, and the Londons theory does not hold. The corresponding generalization of this theory near T_c is the Ψ-theory [16] which introduces the order parameter—a certain macroscopic wave function Ψ. The free energy density of the superconductor is then written in the form (we immediately take into account a possible anisotropy of the material [37, 38]):

$$F_s = F_{\text{no}} + a|\Psi|^2 + \frac{b}{2}|\Psi|^4 + \frac{1}{4m_l^*}\left|\left(-i\hbar\nabla_l - \frac{2e}{c}\mathbf{A}_l\right)\Psi\right|^2 + \frac{\mathbf{H}^2}{8\pi} \tag{5}$$

Here $\mathbf{H} = \operatorname{rot} \mathbf{A}$ is the magnetic field strength, F_{no} is the free energy density in the normal phase, $a = \mathbf{a}t$, $t = (T - T_c)/T_c$, $b = \text{const}$, the pair charge is assumed to be equal to $2e$ and $2m_l^* = \{2m_x^*, 2m_y^*, 2m_z^*\}$ are the principal values of the mass of superconducting pairs. In the isotropic case (or for crystals with cubic symmetry) $m_x^* = m_y^* = m_z^* = m^*$. Since $|\Psi|^2$ is not a measurable quantity, for m^* or for one of the masses m_i^* we can choose any value, but it is more convenient to assume $m^* = m$ to be the electron mass. It is also convenient to use the notation $\Psi = \sqrt{n_s/2}e^{i\varphi}$ when $|\Psi|^2 = n_s/2$ is pair concentration (in equilibrium without the field $|\Psi|^2 = -a/b = (\mathbf{a}/b)|t|$). the Ψ-theory is presented in a large number of original papers, reviews and books (see, in particular, Ref. [6], as well as [4, 16, 17, 25, 34, 37, 38]). In addition to the remarks to be made below (Sections 5 and 6), I shall touch upon the meaning of the Ψ-function introduced in [16]. In Ref. [16] we find the words: "We may suppose that our function $\Psi(\mathbf{r})$ is directly connected with the density matrix $\rho(\mathbf{r}, \mathbf{r}') = \int \Psi^*(\mathbf{r}, \mathbf{r}_i')\Psi(\mathbf{r}', \mathbf{r}_i')\, d\mathbf{r}_i'$, where $\Psi(\mathbf{r}, \mathbf{r}_i')$ is the true wavefunction of the electrons in the metal, depending on the coordinates of all electrons, $\mathbf{r}_i$ $(i = 1, 2, \ldots, N)$; the $\mathbf{r}_i'$ are the coordinates of all the electrons except the one considered, whose coordinates at two points are taken as $\mathbf{r}$ and $\mathbf{r}'$. It might be thought that when $|\mathbf{r} - \mathbf{r}'| \to \infty$, we have $\rho = 0$ for a non-superconducting body having no long-range order, while in the superconducting state $\rho(|\mathbf{r} - \mathbf{r}'| \to \infty) \to \rho \neq 0$. It is reasonable to suppose now that the density-matrix is connected with our Ψ-function by the relation $\rho(\mathbf{r}, \mathbf{r}') = \Psi^*(\mathbf{r})\Psi(\mathbf{r}')$".

Obviously, the long-range order mentioned here is an off-diagonal long-range order (ODLRO); see e.g. Ref. [25], p. 320 and Ref. [6], §26. So, the concept of ODLRO actually occurs in [16]. I dare make this remark of priority character because this statement is not due to me but to Landau who was the first to introduce the concept of ODLRO in application to a superfluid liquid.

5. The specificity of macrotheory for HTSC

It may seem at first glance that the macroscopic Ψ-theory should hold near T_c, whatever the micro-picture for a given superconductor. But this is, of course, not so. First, the conventional Ψ-theory [16] is the mean-field theory for a second-order phase transition and is therefore invalid in a critical region near T_c. Second, the Ψ-function has been considered above as a complex scalar. Meanwhile, the order parameter can be more complicated, as has already been well-known for a rather long time on an example of superfluid ^{3}He phases. In the case of superconductors, possible order parameters depend on the crystal symmetry, as is discussed in detail in the reviews [39, 40]. If the order parameter is not a complex scalar, then near T_c the macroscopic theory in the mean-field approximation and second-order transition can be developed [39, 40] quite analogously to the simplest scheme of the Ψ-theory to which there corresponds the expression (5). In the case of HTSC materials (as distinguished from superconductors with heavy fermions) no convincing data have as yet been reported concerning the necessity to introduce a non-scalar order parameter or, as is more frequently said, indicative of an unconventional pairing. Furthermore, there is some evidence that pairing in HTSC is a conventional s-pairing and at any rate the order parameter has two components (this is confirmed, for example, by the measurements of the fluctuational part of specific heat in $YBa_2Cu_3O_{7-x}$ near T_c [41]). The order parameter $\mathbf{\Psi}$ is assumed below to have two components as in the known conventional superconductors and in He II.

In addition, in conventional superconductors the mean-field approximation is well applicable since fluctuations are rather small. The latter is due to the fact that the coherent length $\xi_0 = \xi(T = 0)$ is rather large as compared to the atomic scale $d \sim 10^{-7}-10^{-8}$ cm [42]. More concretely, we shall define the critical region, in which fluctuations are large, as the temperature range where $|t| = (T_c - T)/T_c \leqslant t_G$ (for $|t| = t_G$ by definition $\langle|\delta\mathbf{\Psi}|^2\rangle_t/|\mathbf{\Psi}_e(t)|^2 = 1$, where $\delta\mathbf{\Psi}$ are fluctuations of $\mathbf{\Psi}_e(t)$ and $\mathbf{\Psi}_e$ is the equilibrium value of $\mathbf{\Psi}$). Given this [38],

$$t_G = \frac{1}{32\pi^2} \cdot \frac{(k_B T_c b)^2}{\mathbf{a}^4 \xi_x^2(0)\xi_y^2(0)\xi_z^2(0)} = \frac{1}{32\pi^2}\left(\frac{k_B}{\Delta C d^3}\right)^2\left(\frac{d}{\bar{\xi}_0}\right)^6 \tag{6}$$

where $a = \mathbf{a}t$ and b are the coefficients in (5), the coherence length $\xi_l(t) = \xi_l(0)|t|^{-1/2}$, $\xi_l(0) = (\hbar^2/4m_l^* d)^{1/2}$, $\bar{\xi}_0 = \{\xi_x(0)\xi_y(0)\xi_z(0)\}^{1/3}$ and $\Delta C = \mathbf{a}^2/bT_c$ is the specific heat jump at T_c. Obviously, $t_G \propto (\bar{\xi}_0)^{-6}$ depends strongly on $\bar{\xi}_0$, and the small factor $1/32\pi^2 \sim 3 \cdot 10^{-3}$ narrows substantially the critical region. Therefore, even in liquid ^{4}He (i.e., in He II), where $\xi_0 \sim d \sim 3 \cdot 10^{-8}$ cm, we have $t_G \sim 10^{-3}$, that is, $\Delta T_G = t_G T_\lambda = |T_G - T_\lambda| \sim 2 \cdot 10^{-3}$ K. At the same time, in He II one can carry out measurements at $\Delta T_G \lessapprox 10^{-8}$ K, and thus the critical region is widely investigated.

For HTSC, the $\bar{\xi}_0$ value is rather small, say, $\bar{\xi}_0 \sim 10$ Å $= 10^{-7}$ cm, and hence the fluctuations are far stronger than in conventional type I superconductors with $\xi_0 \sim 10^{-5}-10^{-4}$ cm $\gg d$. The estimates for $YBa_2Cu_3O_{7-x}$ lead [38] to the values $t_G \sim 10^{-5}-10^{-4}$, that is, $\Delta T_G = t_G T_c \sim 10^{-2}-10^{-3}$ K. We can hope that in future, for very clean and homogeneous specimens we shall be able to work in such a region too. Moreover, somewhat higher t_G values can occur as well, especially in the case when the Schafroth model is applicable (if, like in He II, $t_G \sim 10^{-3}$ then at $T_c \sim 100$ K already $\Delta T_G \sim 0.1$ K). The main thing is that at $|t| \lessapprox t_G$ the mean field approximation is absolutely inapplicable, but fluctuation corrections are significant (say, reach several per cent) in an appreciably wider range of values $|t| \gg t_G$, which reaches several degrees (see, in particular, Refs. [41, 43]). By the way, it is essential that in a region where fluctuations are small (that is, say, the fluctuation correction to the specific heat, δC, is small as compared to the specific heat jump ΔC), the contribution from fluctuations can be calculated on the basis of the mean field theory—in this case the $\mathbf{\Psi}$-theory of superconductivity (see e.g. Refs. [6, 38, 40]).

Thus, even in the case of s-pairing (the scalar order parameter $\mathbf{\Psi}$) the known HTSC possess an important specific feature, namely, small coherent lengths $\xi_l(0)$ and $\bar{\xi}_0$. In addition to the consequence mentioned above, the smallness of $\xi_l(0)$ can have one more important consequence—the change of boundary conditions.

In conventional superconductors, on the boundary between a superconductor and a vacuum or a dielectric there must hold the condition (from here on, the magnetic field is assumed, for simplicity, to be absent; its account is reduced to the substitution of $\partial/\partial x_l - i(2e/\hbar c)A_l$ for $\partial/\partial x_l$)

$$n_l \frac{\partial \Psi}{\partial x_l}\bigg|_s = 0. \tag{7}$$

where $\mathbf{n} = \{n_x, n_y, n_z\}$ is the normal vector to the boundary S, and the value $\partial\Psi/\partial x_l$ is taken on the surface S. In the general case, however, if allowance is made for the surface energy on the boundary (for more details see Ref. [38]),

$$n_l \tilde{\Lambda}_l \frac{\partial \Psi}{\partial x_l}\bigg|_s = -\Psi|_s, \qquad \tilde{\Lambda}_l = \frac{\xi_l^2(0)T_c}{d(T_c - T_{c,s})}, \tag{8}$$

where $T_{c,s}$ is the critical temperature of the boundary S of the superconductor or, more precisely, in the near-surface layer of thickness d (T_c is the critical temperature in the volume). Generally speaking, $\partial\Psi/\partial x_l \sim \Psi/\xi_l(T)$. Consequently, the condition (8) goes over to (7) if $\tilde{\Lambda}_l(T) \gg \xi_l(T)$. If $\tilde{\Lambda}_l(T) \ll \xi_l(T)$, we come to

$$\Psi|_s = 0, \tag{9}$$

which holds for He II (see Refs. [44–46]). As we can see from (8), $\tilde{\Lambda}_l \propto \xi_l^2(0)$, and thus for a very small $\xi_l(0)$ the phenomenological characteristic of the boundary (which is sometimes referred to as the extrapolation length) $\tilde{\Lambda}_l$ is also small, for which reason the condition (9) is more likely to hold. Generally, the solution of equations (in this case equations of the Ψ-theory together with equations for the electromagnetic field) should be based on the condition (8). Probably, we can often restrict ourselves to the usual condition (7), but we cannot be sure of that in advance. In any case, for HTSC the problem of boundary conditions is obviously very topical and should be studied both on the macro- and micro-levels.

6. On the generalized macrotheory of superconductivity valid in the critical region

As has been mentioned above, the critical region is rather narrow in some cases. But this situation is not universal. For example, in the quasi-two-dimensional case (thin films, etc.) the role of fluctuations increases. Moreover, the t_G value (see (6)) is calculated for a concrete quantity, namely, for the ratio $\langle|\delta\Psi|^2\rangle_t/|\Psi_e(t)|^2$. But for other fluctuations, for other quantities, the critical region can be wider (say, due to other numerical coefficients). Next, there can exist substances with a critical region wider than the one given by the above estimates. Finally, the critical region is of particular interest both in the physical and in a broader aspect. This is all known on an example of He II. Suffice it to note that for He II the mean field Ψ-theory [44] has no domain of applicability at all since for $|t| > t_G$ the macrotheory cannot, generally, be used. Indeed, we should not forget that the macrotheory holds only under the condition

$$\xi_l(T) = \frac{\xi_l(0)}{|t|^{1/2}} = \frac{\xi_l(0)T_c^{1/2}}{|T_c - T|^{1/2}} \gg d. \tag{10}$$

For He II the mean interatomic distance $d = 3.57 \cdot 10^{-8}$ cm and the coherence length $\xi_0 = \xi(T = 0) = 1.63 \cdot 10^{-8}$ cm (for specification and more details see Refs. [45, 46]). Consequently, the condition (10) can hold only for $|t| \ll 0.1$. But on the other hand in this case $t_G \sim 10^{-3}$, and thus the ordinary Ψ-theory is almost completely deprived of the domain of applicability. When we take into account the fluctuation corrections which are also significant for $|t| \sim 0.1$, this conclusion becomes still more weighty. Note that the Ψ-theory for He II was proposed [44] in 1958, before the domain of applicability of the mean field approximation was established [42]. Furthermore, experiments have shown that in a good approximation in He II the density of the superfluid part of the liquid $\rho_s(t) = 0.35\ |t|^{2/3}\ \mathrm{g \cdot cm^{-3}}$, whereas in the mean field theory $\rho_s(t) \propto |t|$.

In connection with what has been said there exists an opinion that the behaviour of He II near the λ-point, that is, in the critical region, is not generally accessible for a comparatively simple phenomenological description. For such a description, a whole number of complicated methods (such as scale invariance, renormalization group theory, etc.) is customarily employed. However, I am of the opinion that much can and should be done on the basis of a generalized Ψ-theory [45, 46]. The essence of this theory consists in the following extension of the expression (5) to the free energy density

$$F_s = F_{no} + F_{so} + a_0 t|t|^{1/3}|\Psi|^2 + \frac{b_0}{2}|t|^{2/3}|\Psi|^4$$
$$+ \frac{g_0}{3}|\Psi|^6 + \frac{1}{4m_l^*}\left|\left(-i\hbar\nabla_l - \frac{2e}{c}A_l\right)\Psi\right|^2 + \frac{H^2}{8\pi} \tag{11}$$

Here $\int F_{so}\,dV = (C_0 T_c/2)t^2 \ln|t|$, and the coefficients a and b in (5) are replaced in such a way that in agreement with experiment the equilibrium value $|\Psi|^2$ could have the form $|\Psi_e|^2 \propto \rho_s = \text{const} \cdot |t|^{2/3}$.

The expression (11) is written already for a superconductor, and for an uncharged He II one should put $e = 0$. The extension to superconductors of the expression used in He II is justified by the universality principle according to which the form of the free energy is determined by the transformational properties of the order parameter Ψ. In this case (He II and superconductors) we assume Ψ to be a complex scalar. We may hope that for superconductors with a more complicated order parameter [39, 40] we can act in a similar way. The application of the generalized Ψ-theory to He II yields not bad results [45, 46], although not everything is clear here. Unfortunately, the generalized theories of superfluidity [45, 46] and superconductivity [38] have not drawn much attention, and are practically not being developed. I think that this is to a great extent the question of fashion. If it becomes clear one day that the study of the cirtical region in HTSC is possible and even interesting for practice, the generalized Ψ-theory of superconductivity is sure to become the object of intensive research.

7. Concluding remarks

The theory of superconductivity has a long history. From the creation of the modern theory of metals in normal state (1927–1933 [1, 2]) to the BCS theory [5] nearly 30 years passed. The BCS theory is 34 years old now and its progress is impressive (see e.g. Ref. [20]). At the same time, on an example of the modern state of the microscopic theory of HTSC it is clearly seen how far we are at the present stage from the creation of a more or less complete microtheory of superconductivity. It seems that we might, in fact, expect from such a theory the possibility of predicting the values of T_c and other parameters (say, the critical field $H_c(T)$ and the penetration depth of the field $\delta(T)$) if the composition and structure of the material are given. Today, even the mechanism of superconductivity in known HTSC is disputable, to say nothing of the calculation of the parameters. But active work is now being carried out both for the models [15, 20, 25, 27–29] and on the basis of a more general approach [47].

To make predictions is a difficult and ungrateful task, but I shall take a risk to suppose that by the centenary of superconductivity (i.e. by 2011) the abovementioned goal of microtheory will have been mainly achieved. It is quite possible and probable that even in the near future a noticeable advance both for a number of models and in the field of macrotheory and its applications will be observed.

One of the most important problems which superconductivity faced and is still facing now is an estimation, even rough, of the maximal value $T_{c,\max}$ which can be reached for the critical temperature T_c. The answer to this question obviously played a decisive role in the estimation of the possibility of creating HTSC. The answers were different, but we did not see any special restrictions on T_c [19]. True, it is natural to assume that $T_{c,\max} \ll \Theta_F$ or at any rate $T_{c,\max} < \Theta_F$ (here $\Theta_F = E_F/k_B$ is the Fermi degeneracy temperature for a given metal). Proceeding from such arguments (of course, absolutely rough) we have suggested that $T_{c,\max} \lesssim 300$ K [19, 8]. Since then, nothing has changed in this question. But if before 1986 the experimental value was $T_{c,\max} \approx 24$ K, today we have $T_{c,\max} \approx 125$ K; when some data, even though nonreproducible, are taken into account, the reached T_c values are still higher. That is why I would now agree with the value [21]

$$T_{c,\max} \sim 300\text{–}500 \text{ K}. \tag{12}$$

Reaching such T_c values would mean that we may speak already not only of HTSC but of RTSC (room-temperature superconductors) as well. The importance of this hardly needs any proof.

The estimate (12) is not, of course, the prediction in the proper sense of the word. But in the case of HTSC, before 1986–87 there were also dreams rather than predictions. Now on the place of the dream of HTSC there has come a dream of RTSC—room-temperature superconductors.

REFERENCES

[1] L. HODDESON, G. BAYM and M. ECKERT, Rev. Mod. Phys. *59*, 287 (1987).
[2] A. SOMMERFELD and H. BETHE, Electronentheory der Metalle. Hanbuch der Physik (Springer, Berlin) *24*, 2 (1933).
[3] R. E. PEIERLS, *Quantum Theory of Solids*. Oxford, Clarendon Press (1955).
[4] J. BARDEEN, Hanbuch der Physik *15*, 274 (1956).
[5] J. BARDEEN, L. COOPER and J. SCHRIEFFER, Phys. Rev. *108*, 1175 (1957).
[6] E. M. LIFSHITZ and L. P. PITAEVSKII, *Statistical Physics*. Part 2 (theory of condensed state) Pergamon Press (1980).
[7] F. LONDON, *Superfluids*, vol. 2 (Wiley, New York (1954)).
[8] V. L. GINZBURG, Progress in Low-Temperature Physics *12*, 1 (1989).
[9] L. D. LANDAU, Journ. Phys. USSR *5*, 71 (1941).
[10] V. L. GINZBURG, Physics Today *42*, No. 5, 54 (1989).
[11] V. L. GINZBURG, Usp. Fiz. Nauk *48*, 26 (1952);
Fortsch. der Phys. *1*, 101 (1953).
[12] R. A. OGG, Phys. Rev. *69*, 243 (1946).
[13] M. R. SCHAFROTH, Phys. Rev. *96*, 1149, 1442 (1954); *100*, 463 (1955).
[14] M. R. SCHAFROTH, S. BUTLER and J. BLATT, Helv. Phys. Acta *30*, 93 (1957).
[15] R. MICNAS, J. RANNINGER and S. ROBASZKIEWICZ, Rev. Mod. Phys. *62*, 113 (1990).
[16] V. L. GINZBURG and L. D. LANDAU, Zh. Eksp. Teor. Fiz. *20*, 1064 (1950).
[17] L. P. GORKOV, Zh. Eksp. Teor. Fiz. *36*, 1918 (1959);
Sov. Phys. JETP *9*, 1364 (1959).
[18] G. M. ELIASHBERG, Zh. Eksp. Teor. Fiz. *38*, 966 (1960);
Sov. Phys. JETP *11*, 696 (1960).
[19] *High Temperature Superconductivity*, Eds. V. L. Ginzburg and D. A. Kirzhnits. Consultants Bureau, New York (1982).
[20] J. P. CARBOTTE, Rev. Mod. Phys. *62*, 1027 (1990).
[21] V. L. GINZBURG, Physics Today, *42*, No. 3, 9 (1989);
Evolutional Trends of Physical Science, Springer-Verlag, Berlin (1991).
[22] Q. HUANG *et al.*, Nature, *347*, 369 (1990).
[23] B. BATLOGG, Physica B, *169*, 7 (1991).
[24] N. MOTT, Physica A, *168*, 221 (1990);
Supercond. Sci. Technol. *4*, S59 (1991).
[25] *High Temperature Superconductivity*. Ed. J. W. Lynn. Springer-Verlag, Berlin (1990).
[26] A. A. MIKHAILOVSKY, S. V. SHULGA, A. E. KARAKOZOV, O. V. DOLGOV and E. G. MAKSIMOV, Nature (in press), (1991).
[27] J. FRIEDEL, J. Phys.: Condens. Matter *1*, 7757 (1989).
[28] V. J. EMERY, Physica B, *169*, 17 (1991).
[29] D. H. LEE, Physica B, *169*, 37 (1991).
[30] I. BOZOVIC *et al.*, Preprint (1991). Phys. Rev. Letters (in press).
[31] T. SCHNEIDER and M. FRICK, In *Earlier and Recent Aspects of Superconductivity*, p. 501, Ed. J. G. Bednorz and K. A. Müller. Springer-Verlag, Berlin (1990).
See also Zs. Phys. B. Condensed Matter *80*, 331 (1990); *8*, 337 (1990).
[32] V. L. GINZBURG and D. A. KIRZHNITS, Zh. Eksp. Teor. Fiz. *46*, 397 (1964);
Sov. Phys. JETP *19*, 269 (1964); Sov. Phys.—Doklady *12*, 880 (1968).
V. L. GINZBURG, Physics Letters *13*, 101 (1964).
Physica Scripta, *T27*, 76 (1989).
L. N. BULAEVSKII, V. L. GINZBURG and G. F. ZHARKOV, Sov. Phys. JETP *58*, 994 (1983).
[33] D. SHOENBERG, *Superconductivity*. Cambridge University Press, Cambridge (1952, 1965).
[34] D. R. TILLEY and J. TILLEY, *Superfluidity and Superconductivity*. A Hilger, Bristol (1986).
[35] V. L. GINZBURG, Journ. Phys. USSR *8*, 148 (1944).
[36] V. L. GINZBURG, Supercond. Sci. Technol. *4*, S1 (1991);
more complete: Sov. Phys.—Uspekhi (1991; in press).
[37] V. L. GINZBURG, Zh. Eksp. Teor. Fiz. *23*, 236 (1952).
[38] L. N. BULAEVSKII, V. L. GINZBURG and A. A. SOBYANIN, Zh. Eksp. Teor. Fiz. *94*, 355 (1988).
Sov. Phys.—JETP *68*, 1499 (1988). See also: Physica C, *153–155*, 1617 (1988);
Sov. Phys.—Uspekhi *32*, 277 (1989).
[39] J. F. ANNELT, N. GOLDENFELD and S. R. RENN, In *Physical Properties of High Temperature Superconductors* II, p. 571. Ed. D. M. Ginsberg, World Scientific, Singapore (1990).

[40] J. F. ANNETT. Adv. in Phys. *39*, 83 (1990).
[41] S. E. INDERHEES *et al.*, Phys. Rev. Lett. *66*, 232 (1991).
[42] V. L. GINZBURG, Fiz. Tverd. Tela *2*, 2031 (1960).
Sov. Phys.—Solid State *2*, 1824 (1960).
[43] M. A. HOWSON *et al.*, Phys. Rev. *B41*, 300 (1990).
[44] V. L. GINZBURG and L. P. PITAEVSKII, Zh. Eksp. Teor. Fiz. *34*, 1240 (1958).
Sov. Phys.—JETP *7*, 858 (1958).
[45] V. L. GINZBURG and A. A. SOBYANIN, Sov. Phys. Uspekhi *19*, 773 (1976);
Sov. Phys.—Uspekhi *31*, 289 (1988);
J. Low Temp. Phys. *49*, 507 (1982);
J. Appl. Phys. Japan *26*, Suppl. 26–3, 1785 (1987).
[46] V. L. GINZBURG and A. A. SOBYANIN, In *Superconductivity*, *Superdiamagnetism*, *Superfluidity*, p. 242, Ed. V. L. Ginzburg. MIR Publishers, Moscow (1987).
[47] O. V. DOLGOV, D. A. KIRZHNITS and E. G. MAKSIMOV, see ref. 46, p. 18.