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Details of the thermodynamical derivation of the Ginzburg–Landau equations

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Abstract
We examine the procedure for the thermodynamical derivation of the Ginzburg–Landau equation for current, which is given unclear and contradictory interpretations in existing textbooks. We clarify all the steps of this procedure and find, as a consequence, a limitation on the validity range of the thermodynamic Ginzburg–Landau theory that has not previously been explicitly stated. We conclude that the thermodynamic theory is applicable only to a superconducting specimen that is not part of an external current-carrying loop.

1. Motivation

The Ginzburg–Landau theory of superconductivity was developed five decades ago and proved to be a powerful and fruitful method [1, 2]. However, derivation of its main equations from the free energy of a superconductor was only briefly described in the original paper [3], and some basic points of this procedure are still not completely understood. Standard textbooks [4–8] give no answer or contain contradictory answers to questions such as the following. What is the sense of the free energy variation with respect to the vector potential of the magnetic field? Why must the result of this variation be zero within a superconductor? Why should one take the variation with respect to the vector potential but not with respect to magnetic induction? Why should a surface integral that appears in the process of the variation be omitted?

In this paper we are going to clarify these points and we hope that the physical assumptions that lie at the basis of the thermodynamical Ginzburg–Landau theory will hence become clearer. Our analysis also shows a restriction on the area covered by the thermodynamic theory, which has not, so far, been explicitly stated.

The fact that the Ginzburg–Landau equations can also be derived from the microscopic theory [9] (see also [4]) does not reduce the importance of the thermodynamic theory. Indeed, in practical calculations the Ginzburg–Landau equations are often used in combination with the Ginzburg–Landau free energy of the superconductor. This approach needs, however, a proper understanding of the interconnections between the equations and the free energy. So one comes again to the questions formulated above.

2. Thermodynamics in magnetic field

Let us first remind the reader of the standard thermodynamics of magnetic substances subject to a magnetic field (see, for example, [10]). It is convenient to assume that the field is produced by a combination of electromagnets connected to some external sources and fed by them. The magnetic part of a free energy differential equals the work δR of these sources necessary to change the field by a small variation $\delta\mathbf{B}(\mathbf{r})$, provided that the temperature of the magnetic sample remains constant and mechanical work is absent. The external sources work on both the field and the sample itself: both have their energies, which cannot be separated because the sample and the field interact. So the sample and the magnetic field constitute our system, and we are looking for their joint free energy.

It is more convenient to calculate first not δR itself but the opposite quantity, that is, the work of the changing field on the currents in the magnets or, more precisely, on the external sources of these currents. The Lorentz force itself cannot work, because it is always perpendicular to the current:

$$f_{\mathrm{L}} = \frac{1}{c}[\mathbf{j} \times \mathbf{B}] \perp \mathbf{j}.$$

However, when a magnetic field is varied, a vortex electric field appears, in agreement with the Maxwell equation

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

This field can work, and its work on the currents during a short time δt equals

$$\delta t \int \mathrm{d}^3 r\, \mathbf{jE}.$$

The work of the currents or their sources on our system—the sample and the field—has the same absolute value but the opposite sign:

$$\delta R = -\delta t \int \mathrm{d}^3 r\, \mathbf{jE}. \tag{2}$$

This formula gives simultaneously the free energy differential δF of our system. Let us transform it using the Maxwell equation

$$\mathbf{j} = \frac{c}{4\pi}\,\mathrm{rot}\,\mathbf{H}.$$

Then we have

$$\delta F = -\delta t \frac{c}{4\pi} \int \mathrm{d}^3 r\, \mathbf{E}\,\mathrm{rot}\,\mathbf{H}.$$

As in (2), the integral here is taken over the volume of the conductors carrying the current. However, we will assume that the integration goes over the whole infinite space, which is more convenient for further calculations. This makes no difference because $\mathrm{rot}\,\mathbf{H} = 0$ outside the wires of the electromagnets.

Because

$$\mathrm{div}[\mathbf{a} \times \mathbf{b}] = \mathbf{b}\,\mathrm{rot}\,\mathbf{a} - \mathbf{a}\,\mathrm{rot}\,\mathbf{b} \tag{3}$$

one obtains, taking $\mathbf{a} = \mathbf{E}$ and $\mathbf{b} = \mathbf{H}$, that

$$\delta F = \delta t \frac{c}{4\pi} \int \mathrm{d}^3 r\, \mathrm{div}[\mathbf{E} \times \mathbf{H}] - \delta t \frac{c}{4\pi} \int \mathrm{d}^3 r\, \mathbf{H}\,\mathrm{rot}\,\mathbf{E}. \tag{4}$$

The first integral can be transformed into a surface one over a boundary of the infinite integration volume, that is, over an infinite surface. This integral is zero because the fields disappear at an infinite distance from their sources. For the second integral, we eliminate the electric field from it using equation (1) and thus obtain the final formula

$$\delta F = \delta t \int \mathrm{d}^3 r\, \frac{1}{4\pi} \mathbf{H} \frac{\partial \mathbf{B}}{\partial t} = \int \mathrm{d}^3 r\, \frac{\mathbf{H}\delta\mathbf{B}}{4\pi}. \tag{5}$$

The domain of integration here is the whole infinite space.

With the help of (3) this expression can be further transformed to another form:

$$\delta F = \frac{1}{4\pi} \int \mathrm{d}^3 r\, \mathbf{H}\delta\mathbf{B} = \frac{1}{4\pi} \int \mathrm{d}^3 r\, \mathbf{H}\,\mathrm{rot}\,\delta\mathbf{A}$$
$$= \frac{1}{4\pi} \int \mathrm{d}^3 r\, \mathrm{div}[\mathbf{H} \times \delta\mathbf{A}]$$
$$+ \frac{1}{4\pi} \int \mathrm{d}^3 r\, \delta\mathbf{A}\,\mathrm{rot}\,\mathbf{H} = \frac{1}{c} \int \mathrm{d}^3 r\, \mathbf{j}\delta\mathbf{A}. \tag{6}$$

Here $\mathbf{A}$ is the magnetic field vector potential. Both formulae (5) and (6) represent the work of current sources on our system (the sample and the magnetic field).

One can see from (5) and (6) that

$$\frac{\delta F}{\delta \mathbf{B}} = \frac{\mathbf{H}}{4\pi}, \qquad \frac{\delta F}{\delta \mathbf{A}} = \frac{\mathbf{j}}{c}. \tag{7}$$

We will see below that the latter equality is important for the Ginzburg–Landau theory. We remind the reader that $\mathbf{j}$ is the density of the external macroscopic conductivity current that produces the magnetic field and stays in the Maxwell equation

$$\mathrm{rot}\,\mathbf{H} = \frac{4\pi}{c}\mathbf{j}.$$

In other words, $\mathbf{j}$ is the current in the electromagnets.

The formulae obtained in this section are derived from thermodynamics and hence are always valid under the equilibrium conditions.

3. The Ginzburg–Landau free energy and derivation of the equations

As in the Landau theory of second-order phase transitions, the Ginzburg–Landau free energy of a superconductor appears as an expansion in terms of the so-called condensate wavefunction, ψ, that replaces the order parameter for the transition between superconducting and normal states. In the absence of magnetic field, the free energy has the following simple form, typical for a second-order phase transition:

$$F = F_\mathrm{n} + \int \mathrm{d}^3 r \left[\frac{\hbar^2}{4m}|\nabla\psi|^2 + a|\psi|^2 + \frac{b}{2}|\psi|^4\right].$$

Here F_n is the free energy of the sample in the normal state. The first (gradient) term under the integral describes an energy increase in a non-uniform state of the superconductor.

If a magnetic field is applied to the sample, the latter expression is slightly modified:

$$F = F_\mathrm{n} + \int \mathrm{d}^3 r \left[\frac{\hbar^2}{4m}\left|\left(\nabla - \frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\right)\psi\right|^2 + a|\psi|^2 + \frac{b}{2}|\psi|^4 + \frac{B^2}{8\pi}\right]. \tag{8}$$

The structure of the gradient term here follows from the gauge invariance principle. The last term under the integral is a density of the magnetic field energy, which must be added to the terms describing the superconducting transition itself.

As in the preceding section, the integral in the Ginzburg–Landau free energy is taken over the whole infinite space. Of course, the condensate wavefunction is zero outside the superconductor, but the magnetic field energy still exists in the space around it.

The free energy (8) corresponds to a non-equilibrium state of the sample that is characterized by a spatial ψ distribution in a given magnetic field.

To find the equilibrium state of the system, one makes use of the fact that the free energy of a system has a minimum in the equilibrium state as compared to its value in any non-equilibrium state, provided that the temperature is fixed and no work is performed on the system.

The parameter that describes an internal state of a superconductor is ψ. Hence the equilibrium condition can be found easily by means of taking the free energy variation with respect to ψ or its complex conjugate ψ^* at given $\mathbf{B}(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$ space distributions, and setting the result equal to zero. As the magnetic field is fixed, no work is performed on the system, which is evident from (5) and (6).

Taking the variation, for example, with respect to ψ^*, one finds

$$\delta F = \int_{V_s} \mathrm{d}^3 r \left[a\psi\delta\psi^* + b|\psi|^2\psi\delta\psi^* + \frac{\hbar^2}{4m}\left(\nabla\psi - \frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\psi\right)\left(\nabla\delta\psi^* + \frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\delta\psi^*\right)\right].$$

As all terms here are proportional to ψ, the integral reduces to the volume of the superconductor, V_s. Integrating the term containing $\nabla\delta\psi^*$ by parts, one obtains

$$\begin{aligned}
&\int_{V_s} \mathrm{d}^3 r \left(\nabla\psi - \frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\psi\right)\nabla\delta\psi^* + \int_{V_s} \mathrm{d}^3 r \left(\nabla\psi - \frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\psi\right)\frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\delta\psi^* \\
&= \oint_{\sigma_s} \mathrm{d}\boldsymbol{\sigma}\,\delta\psi^*\left(\nabla\psi - \frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\psi\right) - \int_{V_s} \mathrm{d}^3 r\,\delta\psi^*\nabla\left(\nabla\psi - \frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\psi\right) + \int_{V_s} \mathrm{d}^3 r\,\frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\delta\psi^*\left(\nabla\psi - \frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\psi\right) \\
&= \oint_{\sigma_s} \mathrm{d}\boldsymbol{\sigma}\,\delta\psi^*\left(\nabla\psi - \frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\psi\right) - \int_{V_s} \mathrm{d}^3 r\,\delta\psi^*\left[\nabla^2\psi - \frac{2\mathrm{i}e}{\hbar c}\nabla(\mathbf{A}\psi) - \frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\nabla\psi + \left(\frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\right)^2\psi\right] \\
&= \oint_{\sigma_s} \mathrm{d}\boldsymbol{\sigma}\,\delta\psi^*\left(\nabla\psi - \frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\psi\right) - \int_{V_s} \mathrm{d}^3 r\,\delta\psi^*\left(\nabla - \frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\right)^2\psi,
\end{aligned}$$

where σ_s is the surface of the superconductor. Now we substitute the result back into the previous expression:

$$\delta F = \int_{V_c} \mathrm{d}^3 r \left[a\psi\delta\psi^* + b|\psi|^2\psi\delta\psi^* - \frac{\hbar^2}{4m}\delta\psi^*\left(\nabla - \frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\right)^2\psi\right] + \frac{\hbar^2}{4m}\oint_{\sigma_s} \mathrm{d}\boldsymbol{\sigma}\,\delta\psi^*\left(\nabla\psi - \frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\psi\right).$$

There are two contributions to the variation, the bulk term and the surface one. Taking into account that the superconducting specimens may have arbitrary sizes and shapes, one can hardly expect that any compensation of these two terms will ever happen. So each one must be set equal to zero independently of the other.

Let us first consider the volume integral. One can suppose it to be more important for a macroscopic body. The corresponding variation must be zero, and because $\delta\psi^*$ in the bulk is an arbitrary function, the following condition must take place in the equilibrium state to minimize the volume contribution to the free energy:

$$-\frac{\hbar^2}{4m}\left(\nabla - \frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\right)^2\psi + a\psi + b|\psi|^2\psi = 0\,. \qquad (9)$$

This is the first Ginzburg–Landau equation. As one can see from the derivation, the equation is an equilibrium condition for the system with the free energy (8).

Now let us consider the surface term in the free energy variation. Generally, it is of less importance, because surface effects are usually small in macroscopic bodies, that is, in the macroscopic limit. However, if a media surrounding the superconductor does not influence electrons in the latter, which is true for a vacuum or a dielectric, then $\delta\psi^*$ may take arbitrary values at the surface. Then one can see that to eliminate the surface integral, the condensate wavefunction at the surface of the semiconductor must satisfy the boundary condition

$$\left[\left(\nabla - \frac{2\mathrm{i}e}{\hbar c}\mathbf{A}\right)\psi\right]_\perp = 0,$$

where the subscript stands for the component of the vector perpendicular to the surface.

Let us note for completeness that the boundary condition at the boundary of a superconductor and a normal metal was found by de Gennes [4] (see also [11]), but its derivation lies outside the thermodynamic theory we consider in this paper.

Now we have to turn to the next step that Ginzburg and Landau performed in their original work. They took the free energy variation with respect to the vector potential $\mathbf{A}$ and set the result equal to zero. This action may not be as clear as the preceding calculations, because in contrast to ψ, $\mathbf{A}$ is not an internal variable of the superconductor, which can be varied without any restrictions. The magnetic field is produced by external electromagnets, and it must satisfy the Maxwell equations. This restricts the possible vector potential variations.

As far as we know, no explanation of this point has ever been given. In some textbooks the words from the original article were simply reproduced without any comments, whereas other authors interpreted this procedure as a minimization with respect to the vector potential.

The latter interpretation seems questionable. First, it is not clear why one has to minimize the free energy with respect to the vector potential but not with respect to the magnetic field itself. These two methods give different results, as is evident from equalities (7).

Second, as was already mentioned above, free energy has a minimum in the equilibrium only when the work of external forces is absent, which implies that the $\mathbf{B}$ space distribution is fixed, see (5). However, Ginzburg and Landau did not use this condition; were it taken into account, it would completely change their variation procedure.

We think that to understand the actual sense of the free energy variation with respect to the vector potential, one has to remember the second of equations (7) that holds in the equilibrium state. The equation shows that at equilibrium this variation is proportional to the density of the current that produces the magnetic field. This current flows in the external electromagnets, and in the separated superconductor sample its density is zero.

Indeed, if one describes the magnetic field in a medium in terms of two fields **B** and **H**, as adopted in the Ginzburg–Landau theory, then the magnetic properties of the medium are characterized by its magnetization which creates the difference between **B** and **H**. The magnetization is connected with local (or 'molecular') currents in the media, whereas **H** is produced by the conductivity current that is absent in the sample if the latter is not connected to the external current-carrying loop.

Hence equation (7) within the superconductor takes the form

$$\frac{\delta F}{\delta \mathbf{A}} = 0, \tag{10}$$

and this is just the condition that Ginzburg and Landau use. It is a general equality that is satisfied at equilibrium in any insulated magnetic substance and that is not specific to a superconductor.

Note that it is based on the fact that the sample is not connected to the external power supply, so that the sample carries no external current. Consequently, all current in the superconducting sample can be treated as a local ('molecular') one that produces magnetization but does not affect rot **H**.

In contrast, if the superconducting sample were a part of the external current loop, then **j** would not be zero in it, and equation (10) could no longer be applied to the sample.

The fact that the thermodynamic Ginzburg–Landau theory is applicable only to the superconductors that are not included in an external current loop was not explicitly stated in the original work [3] or in later textbooks.

It is worth noting that the existing microscopic derivation of the Ginzburg–Landau equations [9, 4] implicitly contains the same limitation as the thermodynamic theory. In [9] the initial electron Green function corresponds to zero current. In [4], the final basis used in the equation's derivation consists of real electron wavefunctions, which also correspond to the absence of current.

Now let us continue the derivation of the second Ginzburg–Landau equation. A variation of the joint free energy of the superconductor and magnetic field is taken with respect to **A**. Please remember that the volume integral is taken over the whole infinite space:

$$\begin{aligned} \delta F &= \int \mathrm{d}^3 r\, \delta \left\{ \frac{1}{8\pi} (\operatorname{rot} \mathbf{A})^2 + \frac{\hbar^2}{4m} \left(\nabla\psi - \frac{2\mathrm{i}e}{\hbar c} \mathbf{A}\psi \right) \right. \\ &\quad \left. \times \left(\nabla\psi^* + \frac{2\mathrm{i}e}{\hbar c} \mathbf{A}\psi^* \right) \right\} = \int \mathrm{d}^3 r \left\{ \frac{\operatorname{rot} \mathbf{A} \operatorname{rot} \delta\mathbf{A}}{4\pi} \right. \\ &\quad + \frac{\hbar^2}{4m} \delta\mathbf{A} \left[-\frac{2\mathrm{i}e}{\hbar c} \psi \left(\nabla\psi^* + \frac{2\mathrm{i}e}{\hbar c} \mathbf{A}\psi^* \right) \right. \\ &\quad \left. \left. + \frac{2\mathrm{i}e}{\hbar c} \psi^* \left(\nabla\psi - \frac{2\mathrm{i}e}{\hbar c} \mathbf{A}\psi \right) \right] \right\} \\ &= \int \mathrm{d}^3 r \left\{ \frac{\delta\mathbf{A}}{4\pi} \operatorname{rot} \mathbf{B} - \frac{1}{4\pi} \operatorname{div}[\mathbf{B} \times \delta\mathbf{A}] \right. \\ &\quad \left. + \delta\mathbf{A} \left[\frac{\mathrm{i}\hbar e}{2mc} (\psi^* \nabla\psi - \psi \nabla\psi^*) + \frac{2e^2}{mc^2} |\psi| \mathbf{A} \right] \right\}. \end{aligned} \tag{11}$$

Here again the equality (3) was used, with $\mathbf{a} = \operatorname{rot} \mathbf{A}$ and $\mathbf{b} = \delta\mathbf{A}$.

The integral of the second term in (11) is transformed into a surface integral over an infinite surface and disappears. This is a consequence of the fact that the integration in the Ginzburg–Landau free energy is taken over the whole infinite space, and not over the superconducting specimen only.

Now, setting δF equal to zero within the superconductor, one obtains the second Ginzburg–Landau equation:

$$\operatorname{rot} \mathbf{B} = \frac{4\pi}{c} \mathbf{j}, \tag{12}$$

$$\mathbf{j} = -\frac{\mathrm{i}\hbar e}{2m} (\psi^* \nabla\psi - \psi \nabla\psi^*) - \frac{2e^2}{mc} |\psi| \mathbf{A}. \tag{13}$$

As we explained above, it follows from the general equilibrium equality (7).

Let us also consider, for completeness, the space outside the superconducting specimen. Here the free energy variation equals $\mathbf{j}/c$, as follows from the second equation (7). Because in the space outside the sample

$$\mathbf{B} = \mathbf{H},$$

one comes in this region to the equation

$$\operatorname{rot} \mathbf{H} = \frac{4\pi}{c} \mathbf{j},$$

where **j** is the external current density in the electromagnets. This is simply the Maxwell equation, as it should be.

4. Conclusion

So we can conclude that the Ginzburg–Landau equation for current is derived from the general equality

$$\frac{\delta F}{\delta \mathbf{A}} = \frac{\mathbf{j}}{c},$$

where **j** is the current density in the electromagnets that produce the magnetic field. This condition is not specific to superconductors. It is important also that the integral in the Ginzburg–Landau free energy is taken over the whole infinite space so that the magnetic field energy outside the superconductor is also taken into account.

To obtain the Ginzburg–Landau equations from the superconductor free energy, one must set **j**, the external current density, equal to zero within the superconductor sample, which means that the sample is not a part of the external current-carrying loop. To the best of our knowledge, this limitation on the validity range of the thermodynamic Ginzburg–Landau theory has never been explicitly stated.

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