10. Phase transitions

10.1 Description of phase transitions

■ **Classification of phase transitions.** The basic thermodynamic potential in the description of phase transitions is the Gibbs potential $G = \mu N$, because one of the equilibrium conditions – in addition to that the temperature and the pressure are uniform – is that the chemical potential coincides in all coexisting phases.

Phase transitions are traditionally classified by the singular behaviour of the derivatives of the Gibbs potential. If some of these derivatives are discontinuous, the phase transition is of *first order*. If all the first derivatives are continuous, but discontinuities (or worse singularities) appear in the second order derivatives, then we are dealing with a *second order* phase transition. These names suggest generalization according to the behaviour of higher derivatives, but this line of classification could not be consistently extended.

■ **Order parameter.** Another popular classification scheme emphasizes the behaviour of the central quantity in the modern theory of phase transition, viz. the *order parameter*. This is a quantity, which by definition is zero in one phase and assumes finite values in the other. In spite of the loose definition, in most cases there is a natural choice for the order parameter. In the gas-liquid transition, for instance, such a natural choice is the difference between the densities of liquid and gas, whereas in the paradigmatic ferromagnetic transition the order parameter is the magnetization. If the change of the order parameter in the phase transition is finite, then we are dealing with a *discontinuous phase transition*. If the order parameter tends to the zero value or departs from it in a continuous fashion, then a *continuous phase transition* takes place.

It is typical of the continuous phase transitions that the order parameter, various response functions and correlation functions exhibit non-analytic behaviour as functions of thermodynamic variables in the vicinity of the *critical point*, i.e. the point of the continuous phase transition in the space spanned by the thermodynamic variables. This non-analytic behaviour is usually a powerlike dependence in deviations from the critical-point values of variables such as the temperature and some ”external field” like the pressure in the gas-liquid transition or the magnetic field strength in the ferromagnetic transition. The exponents appearing in such asymptotic relations are the *critical exponents* (or critical indices) of the transition. The most common critical exponents will be defined and calculated below within the Landau theory of phase transitions.

In many cases phase transitions involve changes in symmetries of the system, which are called *symmetry breaking*. In the ferromagnetic transition, for instance, in the paramagnetic phase the material is often macroscopically isotropic and thus possesses the three-dimensional rotational symmetry. In the ferromagnetic phase the direction of the macroscopic magnetization establishes a preferred direction and the rotational symmetry remains at most in the plane perpendicular to the direction of the magnetization.

■ **Symmetry breaking and order parameter.** It is typical of a second order (or continuous) phase transition that some symmetry of the (usually) high-temperature phase is spontaneously broken in the low-temperature phase. The degree of symmetry breaking may be described by an order parameter vanishing in the *symmetric* (usually) high-temperature phase, but finite in the *ordered* phase with the broken symmetry. Examples:

- Structural transformation of a crystal lattice. In barium titanate (Fig.) electric polarization is brought about, this is ferroelectricity. The polarization $\boldsymbol{P}$ is the natural order parameter.

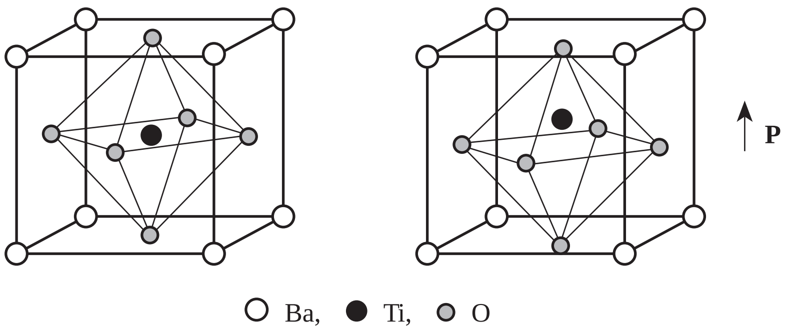

Figure 10–1: Structural transformation of $BaTiO_3$. The polarization $\boldsymbol{P}$ is the order parameter.

- Ferromagnetic phase transition. The broken symmetry is the spin rotation symmetry. Below the critical temperature magnetization $\boldsymbol{M} \neq 0$ appears; this is the order parameter of the system.

- Superconducting transition of electron system and superfluidity transition of ^{4}He. Here, a *gauge symmetry* related with the particle number conservation is broken.

- Symmetry breaking of the electroweak interaction in particle physics. A gauge symmetry is broken here as well.

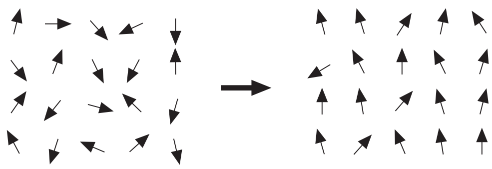

Figure 10–2: Magnetic ordering.

■ **Universality.** It is a remarkable feature of the continuous phase transitions that they are largely insensitive to material properties of the system apart from such global features like rotational or other symmetries. Physically different phase transitions may be described in a unified fashion as soon as important global properties such as the number of components and the tensor character of the order parameter, symmetries of the system and the space dimension are found to be the same. This is the *universality* of continuous phase transitions, and identification of the *universality class* of the particular phase transition is one of the important tasks of its analysis. Most importantly, the values of critical exponents turn out to coincide fairly accurately in physically different systems belonging to the same universality class.

■ **Singularities in the thermodynamic limit.** Mathematical description of continuous phase transitions is much more difficult than that of the discontinuous transitions. In the latter case different phases have chemical potentials of their own and at the phase transition the coexistence condition $\mu_1 = \mu_2$ holds. On the other hand, by definition of the first-order transition, e.g.,

$$\frac{\partial \mu_1}{\partial T} \neq \frac{\partial \mu_2}{\partial T}$$

so that rising or lowering the temperature across the transition temperature necessarily involves a reversal in the ordering of the chemical potentials and in equilibrium the phase corresponding to the minimum of the chemical potential prevails. Chemical potentials of different phases are smooth functions of the state variables.

In case of continuous phase transition, on the contrary, the number of state of equilibria changes: a single chemical potential corresponds to the symmetric phase, whereas several (even infinitely many in case of breaking of a continuous symmetry) chemical potentials of equal value but different values of the order parameter are available for the ordered phase. This is a singularity which is hard to find in the statistical ensembles, whose partition functions, say $Z = \mathrm{Tr}\, \mathrm{e}^{-\beta \widehat{H}}$ are smooth functions of parameters, at least in a finite system with the physically prevailing effectively short-range interactions (Coulomb force is screened is electrically neutral systems, and gravity is small).

In the thermodynamic limit, however, singular behaviour may follow for suitable values of parameters, as was seen in the case of Bose condensation. Other possible sources of singularity are long-range interactions and zero-temperature limit, on which, however, we shall not dwell here. Exact results for physically interesting interacting systems are rare, therefore more or less phenomenological approaches are popular in description of continuous phase transitions. The most general approach, based on a variational principle, is that of the Landau theory.

10.2 Landau theory

■ **Effective thermodynamic potential.** At the critical point (point of the continuous phase transition in the parameter space) the order parameter vanishes in a continuous manner, when the symmetric phase is approached. In the Landau theory the order parameter φ is considered a macroscopic variable describing an incomplete equilibrium, whose equilibrium value is found by minimizing the proper thermodynamic potential.

The system is considered to be so close to the critical point that the order parameter is already small but still so far from the critical point that the system may be assumed to homogeneous and the thermodynamic potential a smooth function of the order parameter and state variables. The thermodynamic potential is then expanded in powers of the order parameter and the leading terms retained. Thus

$$G(p,T,\varphi) = G_0(p,T) + \alpha\varphi + A\varphi^2 + C\varphi^3 + B\varphi^4 + \dots \tag{10.1}$$

The linear term must vanish in case of vector order parameter for a rotation-invariant Gibbs potential. The third-order term gives rise to a discontinuous transition, so that in case of continuous transition only the second and fourth order terms remain. To guarantee existence of equilibrium, the coefficient $B >$, and, although a function of p and T may usually be considered constant. For $A > 0$ the only minimum of (10.1) is $\varphi = 0$, whereas in case $A < 0$ a twofold degenerate nonvanishing solution for the minimum exists. The borderline value $A = 0$ then corresponds to the point of phase transition. The simplest smooth temperature dependence is $A = a(T - T_c)$.

■ **Ferromagnetic ordering.** Here, the basic idea of Landau theory is demonstrated in the example of the prototypical ferromagnetic transition. Denote magnetization by $\boldsymbol{m}$ to emphasize that it is an order parameter assuming values different from the equilibrium magnetization. In relations

$$dU_{\rm sys} = TdS + \mu_0 V\boldsymbol{h}\cdot d\boldsymbol{m}\,, \tag{10.2a}$$
$$dF_{\rm sys} = -SdT + \mu_0 V\boldsymbol{h}\cdot d\boldsymbol{m}\,, \tag{10.2b}$$

the quantity $\boldsymbol{h} \equiv \boldsymbol{h}(T,\boldsymbol{m})$ is the derivative of the thermodynamic potential with respect to the order parameter. In equilibrium, however, it must be equal to the magnetic field strength $\boldsymbol{H}$. The natural parameters of the free energy are T and $\boldsymbol{m}$, i.e. $F_{\rm sys} = F_{\rm sys}(T,\boldsymbol{m})$. If the system is coupled to a magnetic field with the fixed field strength $\boldsymbol{H}$, then the equilibrium value of the magnetization $\boldsymbol{m}$ is determined by the condition that the Gibbs function has a minimum. The magnetic Gibbs potential now becomes an order-parameter dependent function

$$G_{\rm sys}(T, \boldsymbol{H}\,; \boldsymbol{m}) = F_{\rm sys}(T, \boldsymbol{m}) - \mu_0 V \boldsymbol{H} \cdot \boldsymbol{m}\,. \tag{10.3}$$

Choose $\boldsymbol{m}$ to minimize G: $\delta G/\delta \boldsymbol{m} = \delta F_{\rm sys}/\delta \boldsymbol{m} - \mu_0 V \boldsymbol{H} = \mu_0 V \boldsymbol{h} - \mu_0 V \boldsymbol{H} \to 0$. In equilibrium we must have $\boldsymbol{h}(T, \boldsymbol{m}) = \boldsymbol{H}$. In other words, $\boldsymbol{m} = \boldsymbol{m}(T, \boldsymbol{H}) \equiv \boldsymbol{M}$ is the equilibrium magnetization and the familiar result holds

$$dG_{\rm sys} = -SdT - \mu_0 V \boldsymbol{M} \cdot d\boldsymbol{H}. \tag{10.4}$$

In an isotropic system the free energy F depends on the magnitude of the order parameter $m = |\boldsymbol{m}|$. Expand F as power series

$$\boxed{F(T, m) = F_0(T) + \alpha_2(T) m^2 + \frac{1}{2}\alpha_4(T) m^4 + \cdots\,.} \tag{10.5}$$

Assume simplest possible smooth dependencies to provide stable minima in the vicinity of T_c:

$$\begin{aligned} \alpha_2(T) &= a \cdot (T - T_c)\,; \quad a > 0 \\ \alpha_4(T) &= b = \text{ const } > 0 \end{aligned} \tag{10.6}$$

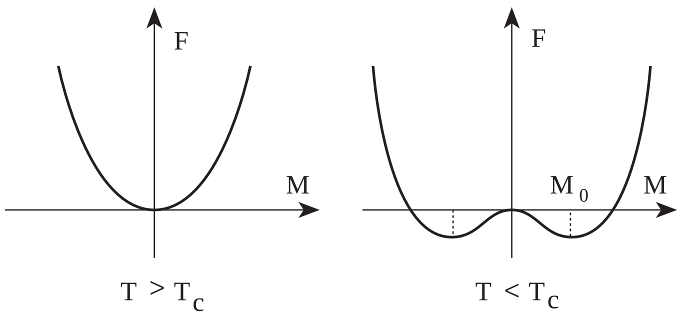

Figure 10–3: Free energy as a function of the order parameter in Landau theory.

Let first $H = 0$. Then the minimum of G is also the minimum of F. From the condition

$$\frac{\partial F}{\partial m} = 2a(T - T_c) m + 2bm^3 = 0$$

the equilibrium magnetization is found as (cf. Fig. 10–3)

$$\begin{aligned} M_0(T) &= 0, & T > T_c \\ M_0(T) &= \pm\sqrt{\frac{a}{b}(T_c - T)}\,. & T < T_c \end{aligned} \tag{10.7}$$

The latter relation determines the value of the *critical exponent* β, which describes the non-analytic behaviour of the order parameter φ as a function of the temperature near the critical point as

$$\varphi(T) \sim (T_c - T)^{\beta}\,, \qquad T < T_c\,, \quad H = 0\,. \tag{10.8}$$

Thus, in the Landau theory $\beta = \frac{1}{2}$.

The spontaneous magnetization $M_0(T)$ is depicted in Fig. 10–4. The minimum value of the zero-field free energy is thus

$$\begin{aligned} F(T, M_0) &= F_0(T)\,; & T > T_c \\ F(T, M_0) &= F_0(T) - \frac{a^2}{2b}(T_c - T)^2\,; & T < T_c \end{aligned} \tag{10.9}$$

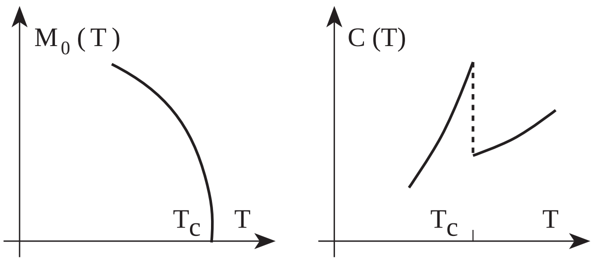

Figure 10–4: Magnetization and heat capacity.

■ **Heat capacity.** According to the definition

$$C_H = T\left(\frac{\partial S}{\partial T}\right)_H = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_H .$$

In zero field $G = F$, more accurately $G(T, H = 0) = F(T, M_0(T))$, yielding $C_H(H = 0) = -T(d^2F/dT^2)$. From relations (10.9) we obtain

$$\begin{aligned} T > T_c: &\qquad C_H(T) = C_0(T) \equiv -T\frac{d^2F_0}{dT^2} \\ T < T_c: &\qquad C_H(T) = C_0(T) + \frac{a^2}{b}T \end{aligned} \tag{10.10}$$

The specific heat has a jump

$$C_H(T_c^-) - C_H(T_c^+) = \frac{a^2}{b}T_c$$

at the critical temperature (Fig. 10–4).

In general, however, the singular behaviour of the heat capacity in a continuous transition is characterized by the critical exponents α and α'

with the definition

$$C_H(T) \sim \begin{cases} (T-T_c)^{-\alpha}\,, & T > T_c\,, \\ (T_c-T)^{-\alpha'}\,, & T < T_c\,, \end{cases} \qquad H = 0\,, \tag{10.11}$$

where usually both α and α' are numerically small. The finite discontinuity in the Landau theory in these terms is described by putting $\alpha = \alpha' = 0$.

■ **Susceptibility.** If the external field $\boldsymbol{H} \neq 0$, we arrive at the equilibrium condition

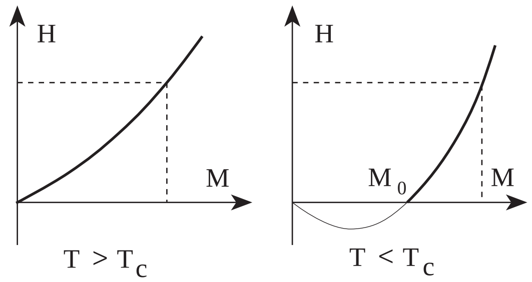

Figure 10–5: Determination of the equilibrium magnetization, relation (10.13).

$$\frac{\partial G}{\partial \boldsymbol{m}} = 0 \;\Leftrightarrow\; \frac{\partial F}{\partial \boldsymbol{m}} = \mu_0 V \boldsymbol{H}\,, \tag{10.12}$$

i.e., according to relations (10.5) and (10.6),

$$2a(T-T_c)M + 2bM^3 = \mu_0 V H\,. \tag{10.13}$$

In case $T > T_c$ (Fig. 10–5) in the limit of small field H the magnetization $M = \chi H + \mathcal{O}(H^3)$, with the susceptibility χ

$$\chi = \frac{\mu_0 V}{2a(T-T_c)}\,. \tag{10.14}$$

In case $T < T_c$ in the limit of small H obviiously (cf. Fig. 10–5) $M = M_0 + \delta M$, where $\delta M \propto \delta H$ is small. The following relation holds,

$$\begin{aligned} \mu_0 V \delta H &= 2a(T-T_c)\delta M + 6b{M_0}^2 \delta M \\ &= 2a(T-T_c)\delta M + 6b\frac{a}{b}(T_c - T)\delta M \\ &= 4a(T_c-T)\delta M\,. \end{aligned}$$

This yields for the susceptibility the result

$$\chi = \frac{\delta M}{\delta H} = \frac{\mu_0 V}{4a(T_c - T)}\,. \tag{10.15}$$

From relations (10.14) and (10.15) it is seen that the critical exponents γ and γ' of the susceptibility, defined as

$$\chi(T) \sim \begin{cases} (T - T_c)^{-\gamma}\,, & T > T_c\,, \\ (T_c - T)^{-\gamma'}\,, & T < T_c\,, \end{cases} \qquad H = 0\,, \tag{10.16}$$

in the Landau theory assume the value $\gamma = \gamma' = 1$.

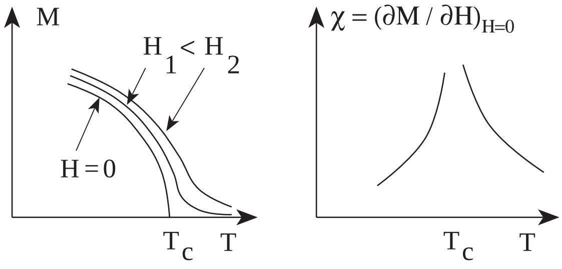

Figure 10–6: Magnetization and susceptibility.

The susceptibility is depicted in Fig. 10–6. In the same plot dependence of the magnetization M on the temperature and field strength H has been sketched. In particular, at the critical temperature $T = T_c$, from the condition $\mu_0 V H = 2bM^3$ it follows

$$M(T_c\,, H) = \text{ const } \times H^{1/3}\,. \tag{10.17}$$

From this relation it follows that the critical exponent δ, which describes the non-analytic dependence of the order parameter φ of the external field h at the critical temperature as

$$\varphi(h) \sim h^{1/\delta}\,, \qquad T = T_c\,, \tag{10.18}$$

in the Landau theory assumes the values $\delta = 3$.

10.3 Ginzburg–Landau theory of superconductivity

In a large system it is possible that the order parameter is not constant throughout the whole volume, especially, when the broken symmetry is continuous. Deviations from homogeneous order parameter are also necessary to describe fluctuations near the critical point. If local variability is allowed, then a field theory is obtained with the order parameter $m(\boldsymbol{r})$ as a function of position. Such a generalization was put forward in V. Ginzburg in application to superconductivity and turned out to be very successful explanation of this phenomenon discovered already in 1911 by H. Kamerlingh–Onnes. The Ginzburg-Landau theory has proved a fruitful starting point for description of several other ordering phenomena as well.

■ **Free energy.** The order parameter is assumed to be a complex-valued function $\Psi(\boldsymbol{r})$ called *macroscopic wave function* in this context. Physically, this is quantity describing the correlated electron pairs (Cooper pairs), whose motion gives rise to the phenomenon of superconductivity in metals. The "genuine" wave function of such a pair of electrons depends on variables of both electrons, of course. The macroscopic wave function here is related to the motion of the center of mass of the Cooper pair, which is thus considered a pointlike object in the Ginzburg-Landau theory. The typical length scale up to which the electrons of the pair remain correlated, the *coherence length* ξ_0 (usually $\xi_0 \gtrsim$ 1000 Å), must therefore be much less than the typical spatial scale of the macroscopic wave function for the Ginzburg-Landau theory to be consistent.

The free energy is written as local functional functional of the macroscopic wave function, where the spatial dependence is taken into account by the leading term of the gradient expansion:

$$F_{\mathrm{sys}}(T,[\Psi]) = \int d^3\boldsymbol{r}\,\left[f_0 + \frac{\hbar^2}{2m^*}\left|\nabla\Psi\right|^2 + a(T-T_c)\left|\Psi\right|^2 + \frac{b}{2}\left|\Psi\right|^4\right]\,. \quad (10.19)$$

Here, m^* is a parameter of dimension of mass. In a system with charged particles in an magnetic field gauge invariance is imposed by replacing the gradient in the canonical momentum operator $-i\hbar\nabla$ by the covariant derivative to obtain $-i\hbar\nabla - e^*\boldsymbol{A}(\boldsymbol{r})$, where $\boldsymbol{A}$ is the vector potential and e^* the charge. With this substitution the Ginzburg-Landau free energy (10.19) remains invariant under the transformation $\Psi(\boldsymbol{r}) \to \Psi(\boldsymbol{r})e^{i\alpha(\boldsymbol{r})}$ even in case of position-dependent $\alpha(\boldsymbol{r})$, when it is accompanied by the proper change of the vector potential. When the energy of the magnetic field is added, the total Ginzburg-Landau free energy is obtained in the form

$$\boxed{F = \int d^3\boldsymbol{r}\left\{f_0 + \frac{\hbar^2}{2m^*}\left|\left(\nabla - \frac{ie^*}{\hbar}\boldsymbol{A}\right)\Psi\right|^2 + a\tau\left|\Psi\right|^2 + \frac{b}{2}\left|\Psi\right|^4 + \frac{\boldsymbol{B}^2}{2\mu_0}\right\},} \quad (10.20)$$

where for brevity the notation $\tau = T - T_c$ has been introduced. Thus, we are dealing with a 4-parameter (m^*, e^*, a, b) phenomenological theory.

■ **Variational conditions.** It is convenient to write down the stationarity equations for the functional (10.20) with the aid of the *functional derivative*, whose definition for an arbitrary functional $F[f]$ of the function $f(\boldsymbol{r})$ is

$$\delta F[f] \equiv \int d^3\boldsymbol{r}\;\delta f(\boldsymbol{r})\,\frac{\delta F}{\delta f(\boldsymbol{r})}\,.$$

In practice, the usual chain rule together with partial integration is sufficient to arrive at expressions containing

$$\frac{\delta f(\boldsymbol{r}')}{\delta f(\boldsymbol{r})} = \delta(\boldsymbol{r}' - \boldsymbol{r})$$

which allows to resolve one spatial integral.

Since the electromagnetic field interacts with charged matter, the vector potential $\boldsymbol{A}$ is a variable quantity as well. Consider first variation of the magnetic field energy with fixed boundary conditions for the fields varied. Then

$$\begin{aligned}\delta \int_V \boldsymbol{B}^2 &= \delta \int_V (\nabla \times \boldsymbol{A}) \cdot (\nabla \times \boldsymbol{A}) = 2 \int_V \boldsymbol{B} \cdot (\nabla \times \delta \boldsymbol{A}) \\ &= -2 \int_V \nabla \cdot (\boldsymbol{B} \times \delta \boldsymbol{A}) + 2 \int_V \nabla \cdot (\boldsymbol{B} \times \delta \boldsymbol{A}_c) \\ &= -2 \int_{\partial V} \boldsymbol{n} \cdot (\boldsymbol{B} \times \delta \boldsymbol{A}) + 2 \int_V \delta \boldsymbol{A} \cdot (\nabla \times \boldsymbol{B}) , \end{aligned} \tag{10.21}$$

where the notation $\delta \boldsymbol{A}_c$ means, that the derivatives in the nabla do not act on this factor. Taking into account the fixed boundary condition, we arrive at the result

$$\frac{\delta}{\delta \boldsymbol{A}(\boldsymbol{r})} \frac{1}{2\mu_0} \int_V \boldsymbol{B}^2 = \frac{1}{\mu_0} \nabla \times \boldsymbol{B} = \nabla \times \boldsymbol{H} .$$

Thus example illustrates sufficiently the calculation of the functional derivatives also for the case of the order parameter Ψ. Therefore, we quote only the final equilibrium conditions.

■ **Superconductivity.** From the requirement of stationarity with respect to variations of $\Psi(\boldsymbol{r})^*$ and $\delta \boldsymbol{A}(\boldsymbol{r})$ the Ginzburg–Landau equations for superconductivity follow

$$-\frac{\hbar^2}{2m^*} \left(\nabla - \frac{ie^*}{\hbar} \boldsymbol{A} \right)^2 \Psi + \left(a\tau + b \left| \Psi \right|^2 \right) \Psi = 0 , \tag{10.22a}$$

$$\boldsymbol{J} \equiv \frac{e^* \hbar}{2im^*} \left[\Psi^* (\nabla \Psi) - (\nabla \Psi^*) \Psi \right] - \frac{(e^*)^2}{m^*} \boldsymbol{A} \left| \Psi \right|^2 = \nabla \times \boldsymbol{H} . \tag{10.22b}$$

The former is a nonlinear Schrödinger equation for superconducting particles with the mass m^* and charge e^*. The latter equation, which determines the supercurrent density $\boldsymbol{J}$, is Ampère's law $\nabla \times \boldsymbol{H} = \boldsymbol{J}$ for static fields. The first term of the current density $\boldsymbol{J}$ is the canonical current, which is not gauge invariant. Only the account of the second term gives rise to a gauge invariant current density.

■ **Temperature-dependent coherence length.** The Ginzburg–Landau equations are nonlinear, therefore an exact solution is possible only in special cases. If there is no magnetic field, it is consistent to put $\boldsymbol{A} = 0$ everywhere. Relation (10.22b) is then automatically fulfilled, if Ψ is real.

Consider a superconductor filling the half-space $x > 0$. Then Ψ is a function of x only and the equation (10.22a) assumes the form

$$-\frac{\hbar^2}{2m^*} \frac{d^2 \Psi(x)}{dx^2} + a\tau \Psi(x) + b\Psi(x)^3 = 0 . \tag{10.23}$$

As a boundary condition, impose $\Psi(0) = 0$. The equation may be solved by multiplying by the factor $\Psi'(x)$ and constructing a first integral. The first-order differential equation obtained is also solvable. It turns out that a meaningful solution may only be found for temperatures $\tau < 0$, i.e. $T < T_c$. For the order parameter the expression

$$\Psi(x) = \sqrt{n_s}\tanh\frac{x}{2\xi}\,; \quad (x > 0), \tag{10.24}$$

follows, where

$$n_s = -\frac{a\tau}{b} \tag{10.25}$$

and

$$\xi = \frac{\hbar}{\sqrt{2am^*(T_c - T)}}\,. \tag{10.26}$$

The constant $n_s = |\Psi(\infty)|^2$ is the density of superconducting particles. The quantity ξ, which describes the thickness of the surface layer, is the *temperature-dependent coherence length.*. This is the typical length scale of the Ginzburg-Landau model. It is approximately equal to the coherence length ξ_0 of the correlated electron pairs far from T_c, but since it diverges as $\sqrt{T_c - T}$ near T_c, it is bound to become much larger than ξ_0 (which is independent of the temperature) close enough to the critical point.

■ **Meissner effect.** In a weak magnetic field the vector potential $\boldsymbol{A}$ and the field strength $\boldsymbol{H}$ are small and the wave function may be formally expanded as

$$\Psi = \Psi_0 + \Psi_1 + \Psi_2 + \dots\,,$$

where Ψ_0 is the zero-field solution obtained above, and $\Psi_n \propto |\boldsymbol{A}|^n$.

Let the region $x > 0$ be superconducting, and the magnetic field directed along the y axis. Then

$$\boldsymbol{A} = A(x)\boldsymbol{e}_z\,; \quad \boldsymbol{B} = \nabla\times\boldsymbol{A} = -A'(x)\boldsymbol{e}_y\,.$$

Rewrite equation (10.22a) in more detail,

$$-\frac{\hbar^2}{2m^*}\nabla^2\Psi + \frac{ie^*}{m^*}\boldsymbol{A}\cdot\nabla\Psi + \frac{(e^*)^2}{2m^*}\boldsymbol{A}^2\Psi + \left(a\tau + b|\Psi|^2\right)\Psi = 0.$$

The zeroth order yields the previous equation (10.23). In the first order the vector potential is absent, because the vectors $\boldsymbol{A}$ and $\nabla\Psi_0$ are orthogonal. Thus, $\Psi_1 = 0$, and the change of the wave function is of second order in $\boldsymbol{A}$. Equation (10.22b) then implies that in the first-order accuracy

$$-\frac{(e^*)^2}{m^*}\boldsymbol{A}|\Psi_0|^2 = \nabla\times\boldsymbol{H} = \frac{1}{\mu_0}\nabla\times(\nabla\times\boldsymbol{A}) = -\frac{1}{\mu_0}\nabla^2\boldsymbol{A}\,, \tag{10.27}$$

where the last from is a consequence of the relation $\nabla\cdot\boldsymbol{A} = 0$.

Equation (10.27) is readily solved deep in the superconductor, where $\Psi_0 = \text{cons}$. For the function $A(x)$ with the account of relations (10.24) and (10.26) the following equation is obtained

$$\frac{d^2A(x)}{dx^2} = -\frac{\mu_0(e^*)^2a\tau}{m^*b}A(x)\,. \tag{10.28}$$

The physically meaningful solution is the exponentially falling off function

$$A(x) \underset{x\to\infty}{\longrightarrow} \text{const} \times \exp\left(-\frac{x}{\lambda}\right), \tag{10.29}$$

where the parameter λ is the *penetration depth*

$$\lambda = \sqrt{\frac{bm^*}{a\mu_0(e^*)^2(T_c - T)}}\,. \tag{10.30}$$

Usually, $\lambda \gg 100$ Å. Since deep in the superconductor $\boldsymbol{A} = 0$, the magnetic field does not penetrate the matter. The superconductor is thus a perfect *diamagnet*. This is the *Meissner effect*.

In the Ginzburg-Landau theory both the temperature-dependent coherence length (10.26)and the penetration depth (10.30) diverge in the same way, when the critical temperature is approached. Their temperature-independent ratio

$$\kappa = \frac{\lambda}{\xi} = \frac{m^*}{\hbar e^*}\sqrt{\frac{2b}{\mu_0}}\,, \tag{10.31}$$

the *Ginzburg-Landau parameter* is an important parameter of the theory, since its value determines the sign of the surface tension between the superconducting and normal phases and thus the character of the phase transition between them in strong magnetic fields.

■ **Critical field.** Superconductors thus expel magnetic field. A strong enough magnetic field, however, destroys the superconducting state. The borderline value, the *critical field* H_c may be determined thermodynamically as follows. A superconducting body possesses a magnetic moment $\boldsymbol{m} = V\boldsymbol{M} = -V\boldsymbol{H}$. The potential energy of this magnetic moment in the external field $W = -\mu_0 \int_0^{\boldsymbol{H}} \boldsymbol{m}\cdot d\boldsymbol{H} = -\mu_0\, \frac{1}{2}\, \boldsymbol{m}\cdot\boldsymbol{H} = \frac{1}{2}\, V\mu_0 H^2$ is the energy in excess to the free energy of the superconductor and the energy of the magnetic field in the absence of the superconductor (which occupies the volume of the superconductor as well). The corresponding interaction energy between the magnetic moment of the same body in the normal state and the external field is negligible due to the small numerical value of the dia- and paramagnetic susceptibilities. Therefore, the difference between the energies of the body in the magnetic field in the homogeneous superconducting state and in the normal state is – up to surface effects –

$$F_s - F_n = -V\,\frac{a^2(T_c - T)^2}{2b} + \frac{1}{2}\,V\mu_0 H^2\,. \tag{10.32}$$

Just at the the critical field this difference vanishes, and near the critical temperature the thermodynamic critical field is

$$H_c = \frac{a(T_c - T)}{\sqrt{\mu_0 b}}\,. \tag{10.33}$$

Surface effects, however, turn out to be of paramount significance in many practical superconductors. The point is that the transition from, say, the superconducting to the normal state requires initial nucleation of small normal state formations, and the appearance of these is hindered by the energy cost to build up the surface, when the surface tension between the normal and superconducting states is positive. In such a case of a *superconductor of the I type* the phase transition takes place in fields larger than the thermodynamic critical field so that the magnetic field penetrates a large volume at once (the surface area between the ordinary and superconducting phases is minimized). In a *superconductor of the II type* the surface tension of the interface between the superconducting and normal states is negative, which leads to the nucleation of the normal phase in a superconducting bulk at field strengths less than the thermodynamic critical field (the borderline value is the lower critical field H_{c1}) and to the nucleation of superconducting phase at field strength larger than the thermodynamic critical field (the borderline value is the upper critical field H_{c2}). In these materials nothing remarkable happens at H_c.

In superconductors of the II type the magnetic flux penetrates the superconducting bulk as thin filaments (*vortices*) forming a vortex lattice (Abrikosov lattice). The flux in the filaments is quantized with the flux quantum h/e^*. Observations on this phenomenon as well as on quantization of magnetic flux through a superconducting ring have shown that the charge of the superconducting particle $e^* = -2e$, where $-e$ is the electron charge. The supercurrent is carried by bound pairs of electrons. These Cooper pairs are loose formations with the diameter of the of the coherence length ξ_0 and thus much larger than the distances between the conduction electrons.

The quantization of the magnetic flux may be readily demonstrated in geometries of a superconducting ring in a magnetic field and for a normal-state filament aligned with an external magnetic field in the superconducting bulk. Imagine a closed contour around the filament or along the ring deep in the bulk superconductor so that on the loop the magnetic induction vanishes and the modulus of the order parameter is constant. From relation (10.22b) and the representation $\Psi = |\Psi| \mathrm{e}^{i\phi}$ it then follows that on the contour

$$\nabla\phi = \frac{e^*}{\hbar}\boldsymbol{A} \,. \tag{10.34}$$

Integrating over the closed contour we obtain, by virtue of the Stokes theorem,

$$\Delta\phi = \oint \nabla\phi \cdot d\boldsymbol{l} = \frac{e^*}{\hbar}\oint \boldsymbol{A}\cdot d\boldsymbol{l} = \frac{e^*}{\hbar}\int \boldsymbol{n}\cdot\nabla\times\boldsymbol{A}\, dS = \frac{e^*}{\hbar}\Phi_B \,, \tag{10.35}$$

where $\Delta\phi$ is the change of the phase of the wave function after traversing over the contour and Φ_B is the magnetic flux through a surface, whose boundary is the closed contour at hand. The wave function must, however, be a single-valued function of the position, which imposes the condition

$\Delta\phi = 2\pi n$ with an integer n. Thus, the magnetic flux through a superconducting ring or normal-state filament is quantized as

$$\Phi_B = \int \boldsymbol{n} \cdot \boldsymbol{B}\, dS = \frac{h}{e^*}\, n\,. \tag{10.36}$$

In particular, this condition imposes restrictions on the appearance of normal-state vortices in the phase transition to the normal state in a type II superconductor in magnetic field.

10.4 Fluctuations in Landau theory

Landau theory is based on an effective thermodynamic potential describing the system in incomplete equilibrium described by the order parameter φ. The probability of such a state may be estimated in a manner similar to that used in the Einstein theory of fluctuations. Consider the classical canonical ensemble (for simplicity of notation).

The partition function is the measure of the phase state with the weight $\mathrm{e}^{-\beta H}$:

$$Z = \int' d\Gamma\, \mathrm{e}^{-\beta H(p,q)}\,. \tag{10.37}$$

The measure of the part of the phase state corresponding to the incomplete equilibrium may be written in a similar form by imposing the condition $\varphi = \varphi(p,q)$, where $\varphi(p,q)$ is the order parameter expressed as function of the variables of the phase space. Formally this is effected as

$$Z(\varphi) = \int' d\Gamma\, \delta\left(\varphi - \varphi(p,q)\right) \mathrm{e}^{-\beta H(p,q)}\,. \tag{10.38}$$

Obviously $Z = \displaystyle\int d\varphi\, Z(\varphi)$ and the relative frequency at which the incomplete equilibrium occurs in the phase space is

$$\Pr(\varphi) = \frac{Z(\varphi)}{Z} = \mathrm{e}^{\beta[F - F(\varphi)]}\,, \tag{10.39}$$

where the effective free energy is

$$F(\varphi) = -T \ln Z(\varphi)\,. \tag{10.40}$$

Substituting the expression for $F(\varphi)$ in the Landau theory (inhomogeneous system)

$$F(\varphi) = F_0 + \int d^3\boldsymbol{r}\, \left[g(\nabla\varphi)^2 + a(T - T_c)\varphi^2 + B\varphi^4\right] \tag{10.41}$$

we arrive at the probability density for the order parameter in the form

$$\Pr(\varphi) \propto \mathrm{e}^{-\beta \int d^3\boldsymbol{r} \left[g(\nabla\varphi)^2 + a(T-T_c)\varphi^2 + B\varphi^4\right]}\,. \tag{10.42}$$

Calculations with such a weight are only possible in the form of an expansion in B. The leading order is given by the Gaussian distribution corresponding to $B = 0$. Already in this approximation problems in definition of the mathematical quantities involved appear. For instance, the correlation function of the order parameter is

$$\langle\varphi(\boldsymbol{r})\varphi(\boldsymbol{r}')\rangle = \frac{\displaystyle\int\prod_{\boldsymbol{r}} d\varphi(\boldsymbol{r})\,\varphi(\boldsymbol{r})\varphi(\boldsymbol{r}')\,\mathrm{e}^{-\beta\int d^3\boldsymbol{r}\left[g(\nabla\varphi)^2+a(T-T_c)\varphi^2\right]}}{\displaystyle\int\prod_{\boldsymbol{r}} d\varphi(\boldsymbol{r})\,\mathrm{e}^{-\beta\int d^3\boldsymbol{r}\left[g(\nabla\varphi)^2+a(T-T_c)\varphi^2\right]}}\,. \tag{10.43}$$

In continuum space both the denominator and the numerator consist of a formally infinite-fold integral, to which some meaning should be prescribed. The simplest thing to do is to put the system on a lattice in a finite box, which resricts the integrals over values of the order parameter at different positions to a finite number. In case of a Gaussian integral for a correlation function it is also possible to use the expression (6.51), in which the dimension of the space of integration does not appear explicitly. This means that

$$\langle\varphi(\boldsymbol{r})\varphi(\boldsymbol{r}')\rangle = \frac{T}{2}\left[-g\nabla^2 + a(T-T_c)\right]^{-1}(\boldsymbol{r},\boldsymbol{r}') = \frac{T}{2}\,G(\boldsymbol{r}-\boldsymbol{r}')\,, \tag{10.44}$$

where $G(\boldsymbol{r}-\boldsymbol{r}')$ is the Green function of the operator $-g\nabla^2 + a(T-T_c)$, i.e. the solution of the equation

$$\left[-g\nabla^2 + a(T-T_c)\right]G(\boldsymbol{r}) = \delta(\boldsymbol{r}) \tag{10.45}$$

with vanishing boundary condition at infinity.

More constructively calculation of the correlation function is convenient to carry out in the wave-vector space. Put the system in a, say, cubic box and define the coefficients of the Fourier series as

$$\varphi(\boldsymbol{k}) = \frac{1}{V}\int d^3\boldsymbol{r}\,\mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\varphi(\boldsymbol{r})\,, \tag{10.46}$$

and calculate the Fourier coefficients of the correlation function

$$\frac{1}{V^2}\int d^3\boldsymbol{r}\int d^3\boldsymbol{r}'\,\mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{r}-i\boldsymbol{k}'\cdot\boldsymbol{r}'}\langle\varphi(\boldsymbol{r})\varphi(\boldsymbol{r}')\rangle = \langle\varphi(\boldsymbol{k})\varphi(\boldsymbol{k}')\rangle\,. \tag{10.47}$$

On the other hand, assuming the usual translation invariance we may write

$$\langle\varphi(\boldsymbol{r})\varphi(\boldsymbol{r}')\rangle = C(\boldsymbol{r}-\boldsymbol{r}') \tag{10.48}$$

and

$$\begin{aligned}&\frac{1}{V^2}\int d^3\boldsymbol{r}\int d^3\boldsymbol{r}'\,\mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{r}-i\boldsymbol{k}'\cdot\boldsymbol{r}'}C(\boldsymbol{r}-\boldsymbol{r}')\\ &\quad= \frac{1}{V}\int d^3\boldsymbol{r}'\,\mathrm{e}^{-i\left(\boldsymbol{k}+\boldsymbol{k}'\right)\cdot\boldsymbol{r}'}\frac{1}{V}\int d^3\boldsymbol{r}\,\mathrm{e}^{-i\boldsymbol{k}\cdot\left(\boldsymbol{r}-\boldsymbol{r}'\right)}C(\boldsymbol{r}-\boldsymbol{r}') = \delta_{\boldsymbol{k}',-\boldsymbol{k}}C(\boldsymbol{k})\,.\end{aligned} \tag{10.49}$$

Comparison of relations (10.47) and (10.49) yields

$$\langle\varphi(\boldsymbol{k})\varphi(\boldsymbol{k}')\rangle = \delta_{\boldsymbol{k}',-\boldsymbol{k}}\,\langle\varphi(\boldsymbol{k})\varphi(-\boldsymbol{k})\rangle = \delta_{\boldsymbol{k}',-\boldsymbol{k}}\,\langle|\varphi(\boldsymbol{k})|^2\rangle\,, \tag{10.50}$$

since for a real $\varphi(\boldsymbol{r})$ from (10.46) it follows that $\varphi^*(\boldsymbol{k}) = \varphi(-\boldsymbol{k})$. Express now the Gaussian weight in terms of $\varphi(\boldsymbol{k})$. Substitution of the Fourier series of $\varphi(\boldsymbol{r})$ yields

$$\begin{aligned}\int d^3\boldsymbol{r}\ &\left[g(\nabla\varphi)^2 + a(T-T_c)\varphi^2\right] \\ &= \int d^3\boldsymbol{r}\ \sum_{\boldsymbol{k}}\sum_{\boldsymbol{k}'}\left[-g\boldsymbol{k}\cdot\boldsymbol{k}' + a(T-T_c)\right]\ \varphi(\boldsymbol{k})\varphi(\boldsymbol{k}')\,\mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}+i\boldsymbol{k}'\cdot\boldsymbol{r}} \\ &= V\sum_{\boldsymbol{k}}\left[gk^2 + a(T-T_c)\right]\ |\varphi(\boldsymbol{k})|^2\,. \end{aligned}\tag{10.51}$$

In view of expressions (10.50) and (10.51) it appears convenient to carry out the integration over the real and imaginary parts of $\varphi(\boldsymbol{k})$. These are not all independent variables, since

$$\varphi(\boldsymbol{k}) = \varphi_R(\boldsymbol{k}) + i\varphi_I(\boldsymbol{k}) = \varphi^*(-\boldsymbol{k}) = \varphi_R(-\boldsymbol{k}) - i\varphi_I(-\boldsymbol{k})\,. \tag{10.52}$$

Therefore, it is sufficient to integrate over values of $\varphi_R(\boldsymbol{k})$ and $\varphi_I(\boldsymbol{k})$ in a "half space" of wave vectors, chosen, for instance, by the condition $k_1 \geq 0$. In calculation of the correlation function $\langle|\varphi(\boldsymbol{k})|^2\rangle$ this feature is unimportant, however, because all integrals over values of $\varphi_R(\boldsymbol{k}')$ and $\varphi_I(\boldsymbol{k}')$ with $\boldsymbol{k}' \neq \boldsymbol{k}$ cancel in the expression

$$\langle|\varphi(\boldsymbol{k})|^2\rangle = \frac{\displaystyle\int\prod_{\boldsymbol{k},k_1\geq 0} d\varphi_R(\boldsymbol{k})d\varphi_I(\boldsymbol{k})\ \left[\varphi_R^2(\boldsymbol{k}) + \varphi_I^2(\boldsymbol{k})\right]\ \mathrm{e}^{-\beta V\sum_{\boldsymbol{k}}\left[gk^2+a(T-T_c)\right]|\varphi(\boldsymbol{k})|^2}}{\displaystyle\int\prod_{\boldsymbol{k},k_1\geq 0} d\varphi_R(\boldsymbol{k})d\varphi_I(\boldsymbol{k})\,\mathrm{e}^{-\beta V\sum_{\boldsymbol{k}}\left[gk^2+a(T-T_c)\right]|\varphi(\boldsymbol{k})|^2}}\,. \tag{10.53}$$

Thus, we are left with the following ratio of twofold Gaussian integrals

$$\langle|\varphi(\boldsymbol{k})|^2\rangle = \frac{\displaystyle\int_{-\infty}^{\infty} d\varphi_R(\boldsymbol{k})\int_{-\infty}^{\infty} d\varphi_I(\boldsymbol{k})\ \left[\varphi_R^2(\boldsymbol{k}) + \varphi_I^2(\boldsymbol{k})\right]\ \mathrm{e}^{-\beta V\left[gk^2+a(T-T_c)\right]|\varphi(\boldsymbol{k})|^2}}{\displaystyle\int_{-\infty}^{\infty} d\varphi_R(\boldsymbol{k})\int_{-\infty}^{\infty} d\varphi_I(\boldsymbol{k})\,\mathrm{e}^{-\beta V\left[gk^2+a(T-T_c)\right]|\varphi(\boldsymbol{k})|^2}}\,. \tag{10.54}$$

Calculation yields

$$\langle|\varphi(\boldsymbol{k})|^2\rangle = \frac{T}{V}\,\frac{1}{gk^2 + a(T-T_c)}\,, \tag{10.55}$$

therefore

$$\langle\varphi(\boldsymbol{k})\varphi(\boldsymbol{k}')\rangle = \frac{T}{V}\,\delta_{\boldsymbol{k}',-\boldsymbol{k}}\,\frac{1}{gk^2 + a(T-T_c)}\,. \tag{10.56}$$

We see that the length scale of the correlation function, the *correlation length*, is

$$\xi = \sqrt{\frac{g}{a(T - T_c)}}\,, \qquad T > T_c\,. \tag{10.57}$$

Below T_c a similar relation follows:

$$\xi = \sqrt{\frac{g}{2a(T_c - T)}}\,, \qquad T < T_c\,. \tag{10.58}$$

Therefore, in Landau theory values of the critical exponents of the correlation length

$$\xi(T) \sim \begin{cases} (T - T_c)^{-\nu}\,, & T > T_c\,, \\ (T_c - T)^{-\nu'}\,, & T < T_c\,, \end{cases} \qquad H = 0\,, \tag{10.59}$$

are equal and $\nu = \nu' = \frac{1}{2}$.

Expression for the correlation function as a function of the position vector may now be calculated as the Fourier series

$$\langle \varphi(\boldsymbol{r})\varphi(\boldsymbol{r}')\rangle = \sum_{\boldsymbol{k}}\sum_{\boldsymbol{k}'} \langle \varphi(\boldsymbol{k})\varphi(\boldsymbol{k}')\rangle\, \mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}+i\boldsymbol{k}'\cdot\boldsymbol{r}'} = \frac{T}{V}\sum_{\boldsymbol{k}} \frac{\mathrm{e}^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}}{gk^2 + a(T - T_c)}\,. \tag{10.60}$$

Further, it is customary to pass to the thermodynamic limit, which produces the familiar integral sum and the correlation function may be calculated as the inverse Fourier transform

$$\langle \varphi(\boldsymbol{r})\varphi(\boldsymbol{r}')\rangle = T\int \frac{d^3\boldsymbol{k}}{(2\pi)^3}\, \frac{\mathrm{e}^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}}{gk^2 + a(T - T_c)} = \frac{T}{4\pi g}\, \frac{\mathrm{e}^{-|\boldsymbol{r}-\boldsymbol{r}'|/\xi}}{|\boldsymbol{r}-\boldsymbol{r}'|}\,. \tag{10.61}$$

At the critical temperature $\xi \to \infty$ and

$$\langle \varphi(\boldsymbol{r})\varphi(\boldsymbol{r}')\rangle = \frac{T}{4\pi g|\boldsymbol{r}-\boldsymbol{r}'|}\,, \qquad T = T_c\,, \tag{10.62}$$

which fixes the value of the critical exponent η of the correlation function

$$\langle \varphi(\boldsymbol{r})\varphi(\boldsymbol{r}')\rangle \sim \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|^{1+\eta}}\,, \qquad T = T_c \tag{10.63}$$

in the Landau theory as $\eta = 0$.

10.5 Problems

Problem 10.1. Consider the following expansion in the order parameter ϕ of the Gibbs free energy

$$G(p, T, \phi) = G_0(p, T) + a(T - T_0)\phi^2 - C\phi^3 + B\phi^4\,,$$

where a, B and C are positive constants. Find the equilibrium value of the order parameter, show that there is a first order phase transition in this system and find the transition temperature.

Problem 10.2. Calculate the latent heat of the phase transition in the model of the preceding problem.

Problem 10.3. There are systems in which (on the p,T plane) a line of second-order transitions changes into a line of first-order transitions at the *tricritical* point. Near the tricritical point the Landau expansion of the Gibbs free energy may be written as

$$G(\phi, p, T) = G_0(p, T) + A\phi^2 + B\phi^4 + D\phi^6 \, ,$$

where $D > 0$. The line of second-order transitions is determined by the conditions $A(T_C(p)) = 0$, $B > 0$. On the line of first-order transitions $B < 0$ so that at the tricritical point $A = B = 0$. Find the value of the order parameter on the line of first-order transitions in the ordered phase and establish a connection between A, B and D (which is the equation of the line of first-order transitions).