Geometrical approach to the thermodynamical theory of phase transitions of the second kind

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Abstract

Geometrical approach to the phenomenological theory of phase transitions of the second kind at constant pressure $P$ and variable temperature $T$ is proposed. Equilibrium states of a system at zero external field and fixed $P$ and $T$ are described by points in three-dimensional space with coordinates $\eta$, the order parameter, $T$, the temperature and $\phi$, the thermodynamic potential. These points form the so-called zero field curve in the ($\eta, T, \phi$) space. Its branch point coincides with the critical point of the system. The small parameter of the theory is the distance from the critical point along the zero-field curve. It is emphasized that no explicit functional dependency of $\phi$ on $\eta$ and $T$ is imposed.

It is shown that using ($\eta, T, \phi$) space one cannot overcome well-known difficulties of the Landau theory of phase transitions and describe non-analytical behavior of real systems in the vicinity of the critical point. This becomes possible only if one increases the dimensionality of the space, taking into account the dependency of the thermodynamic potential not only on $\eta$ and $T$, but also on near (local) order parameters $\lambda_i$. In this case under certain conditions it is possible to describe anomalous increase of the specific heat when the temperature of the system approaches the critical point from above as well as from below the critical temperature $T_c$.

1 Introduction

In describing phase transitions occurring in various systems at constant pressure $P$ and variable temperature $T$ (or vice versa) one usually utilizes Gibbs’

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thermodynamic potential \( \Phi = E - TS + PV \), where \( E \) is the internal energy, \( S \) is the entropy and \( V \) is the volume \([1,2]\). Here we shall consider phase transitions of the second kind at constant pressure. In this case \( \Phi \) as a function of the generalized order parameter \( \eta \) has one minimum at \( \eta = 0 \) if \( T > T_c \), whereas if \( T < T_c \) minimum of \( \Phi \) is achieved at finite values of \( \eta = \eta^*_c(T) \).

In many cases \( \Phi \) is an even function of the order parameter:

\[
\Phi(\eta, T, P) = \Phi(-\eta, T, P). \tag{1}
\]

For example, in ferromagnets \( \Phi \) would not change if one simultaneously reversed signs of the order parameter \( \eta = M/M_0 \) (\( M \) is the magnetic moment) and the external field \( h = (\partial \Phi/\partial M)_{P,T} \) \([2,3]\). The same is valid for ferroelectrics. In the case of antiferromagnets \([3]\) and alloys \([4]\) reversing the sign of \( \eta \) is reduced to renaming equivalent sub-lattices. In this article we shall consider the systems for which eq. (1) is valid. The sketch of the dependency of \( \Phi \) on \( \eta \) and \( T \) is shown on Fig.1.

In the absence of the external field and \( T < T_c \) homogeneous equilibrium states corresponding to a given sign of \( \eta \) are achievable only in a system of an infinite size. In real systems of a finite size at \( T < T_c \) the homogeneous phase is unstable and the equilibrium state breaks onto domains corresponding to \( \eta^*_c > 0 \) and \( \eta^*_c < 0 \). The problem about equilibrium dimensions and shapes of domains can be solved only in a theory taking into account microscopic interactions in the system as well as the dimension and the shape of the whole system. The thermodynamical approach does not allow to describe heterogeneous states of a finite system. Our goal is to establish general relations between proprieties of \( \Phi(\eta, T) \) and the behavior of basic thermodynamical parameters of the system, i.e. the order parameter \( \eta^*_c \), the isobaric specific heat \( C_P \) and the isothermal susceptibility \( \chi_T \), in the vicinity of the critical point.

The critical behavior of \( \eta^*_c, C_P, \chi_T \) in the zero external field can be expressed as

\[
C_P = -T \frac{\partial^2 \Phi}{\partial T^2} = a_1(T - T_c)^{-\alpha_1} + a_2(T - T_c)^{-\alpha_2} \cdots, (\alpha_1 > \alpha_2)
\]

\[
\chi_T^{-1} \sim \left( \frac{\partial^2 \Phi}{\partial \eta^2} \right)_{T,P} \propto (T - T_c)^{\gamma}
\]

at \( T > T_c \) and as

\[
C_P = a'_1(T - T_c)^{-\alpha'_1} + a'_2(T - T_c)^{-\alpha'_2} \cdots, (\alpha'_1 > \alpha'_2),
\]
\[ \chi^{-1}_T \propto (T - T_c)^{\gamma'}, \]
\[ \eta \propto (T_c - T)^{\beta}. \]

(3)

at \( T < T_c \). Terms containing \( \alpha_2 \) and \( \alpha'_2 \) are necessary only when \( \alpha_1 = \alpha'_1 = 0 \). In that case indexes \( \alpha_2, \alpha'_2 \) describe critical behavior of \( dC_P/dT \) at \( T \to T_c \pm 0 \).

In order to characterize the system in the “strong” external field at \( T = T_c \) in the vicinity of the critical point one introduces critical indexes \( \delta \) and \( \epsilon \):

\[ \Phi(\eta, T_c) \propto \eta^{\delta + 1}, \]
\[ h = \frac{\partial \Phi}{\partial \eta} \propto \eta^\delta, \]
\[ C_P \propto h^{-\epsilon} \propto \eta^{-\delta \epsilon}, \]

(4)

where \( h \) is the generalized external field [1]. For ferromagnets and ferroelectrics indexes \( \delta, \epsilon \) characterize real behavior of the system for \( h \neq 0 \), whereas for antiferromagnets and alloys they give formal characteristics of \( \Phi(\eta, T) \) in the vicinity of the critical point.

Beside the indexes mentioned above one introduces also indexes describing the behavior of the pair correlation function in the vicinity of the critical point. However, the very concept of pair correlation function is out of the scope of our thermodynamical approach. Therefore, we shall not discuss the corresponding critical indexes.

At first glance, the difference \( T - T_c \) may play the role of a convenient small parameter when one considers phase transitions at constant pressure. However, it is easy to prove that this is not quite true. The definition of the isobaric specific heat is \( C_P = -T(\partial^2 \Phi/\partial T^2)_P \). On differentiating \( \Phi \) twice by temperature we obtain:

\[ \left( \frac{\partial^2 \Phi}{\partial T^2} \right)_P = \frac{\partial^2 \Phi}{\partial T^2} + 2 \frac{\partial^2 \Phi}{\partial \eta \partial T} \left( \frac{d\eta}{dT} \right)_P + \frac{\partial^2 \Phi}{\partial \eta^2} \left( \frac{d\eta}{dT} \right)_P^2 + \frac{\partial \Phi}{\partial \eta} \left( \frac{d^2 \eta}{dT^2} \right)_P, \]

(5)

\[ \frac{\partial^2 \Phi}{\partial \eta \partial T} + \frac{\partial^2 \Phi}{\partial \eta^2} \left( \frac{d\eta}{dT} \right)_P = 0. \]

(6)

Combining eqs. (5), (6) and taking into account that the last term in eq. (6) is identically zero in the case of the zero external field, we obtain:

\[ \left( \frac{\partial^2 \Phi}{\partial T^2} \right)_P = \frac{\partial^2 \Phi}{\partial T^2} - \frac{(\partial^2 \Phi/\partial \eta^2)^2}{\partial \eta^2}. \]

(7)

As one can see from Fig.1 the derivative \( \partial^2 \Phi/\partial \eta^2 \) is positive when \( T > T_c \).
\( \eta = 0 \) and negative when when \( T < T_c, \eta = 0 \). Therefore \(^2\), in the critical point \( \partial^2 \Phi / \partial \eta^2 = 0 \). From the other hand, if \( T > T_c \), then from the condition \( \eta = 0 \) and eq. (1) it follows that \( \partial^2 \Phi / \partial \eta \partial T \equiv 0 \). Therefore, the second term in eq. (7) is zero identically if \( T \to T_c + 0 \). For \( T \to T_c - 0 \) the condition \( h = 0 \) corresponds to the values \( \eta = \eta_* \neq 0 \). In this case the derivative \( \partial^2 \Phi / \partial \eta \partial T \) has, generally, a finite value, thus the second term in eq. (7) is indefinite. Even more inconvenient is the calculation of \( (\partial^3 \Phi / \partial T^3)_P \) which characterizes the behavior of \( dC_P / dT \). One can overcome these difficulties if one chooses such small parameter of the theory of which the thermodynamical values depend smoothly. In the following sections we will show the advantages of the geometrical choice of the small parameter and explain how, in our opinion, a realistic phenomenological theory of phase transitions of the second kind can be built.

2 Geometrical interpretation of phase transitions of the second kind

Let us express the dependency of the thermodynamic potential \( \Phi \) on the order parameter \( \eta \) and the dimensionless temperature \( \tau = T/T_c \) in the form:

\[
\phi = \Phi(\eta, \tau T_c).
\]

Eq. (8) defines a surface in the space \((\eta, \tau, \phi)\). The condition \( h = 0 \)

\[
\Phi_\eta(\eta, \tau T_c) = 0,
\]

where subscript \( \eta \) denotes the appropriate derivative, defines a curve on the surface. Eqs. (8),(9) and the condition \( \Phi_{\eta\eta} > 0 \) define equilibrium states of the system at \( h = 0 \) and constant pressure \( P \).

Consider an arbitrary point on the curve (8),(9) with coordinates \( \eta', \tau', \phi' \). On differentiating eqs. (8),(9) by the length \( s \) of the curve \( (ds^2 = d\eta^2 + d\tau^2 + d\phi^2) \) we obtain:

\[
\Phi_\eta \dot{\eta} + \Phi_\tau \dot{\tau} = \dot{\phi},
\]

\[
\Phi_{\eta\eta} \ddot{\eta} + \Phi_{\eta\tau} \ddot{\tau} = 0 \quad \text{(10)}
\]

\[
\Phi_{\eta\eta} \ddot{\eta} + \Phi_{\eta\tau} \ddot{\tau} = 0 \quad \text{(11)}
\]

2 Later we will show this rigorously
where dot denotes the derivative with respect to $s$: $\dot{\eta}$, $\dot{\tau}$ and $\dot{\phi}$ satisfy the normalizing condition

$$\dot{\eta}^2 + \dot{\tau}^2 + \dot{\phi}^2 = 1. \quad (12)$$

Eqs. (10), (11), (12) determine $\dot{\eta}$, $\dot{\tau}$, $\dot{\phi}$ in an arbitrary point on the curve $h = 0$. Further differentiation of these equations allows us to determine the derivatives of $\eta, \tau, \phi$ of any order. They are expressed in terms of derivatives of $\Phi(\eta, \tau T_c)$ in the the point $\eta', \tau', \phi'$. In the vicinity of this point the increments of the variables can be expressed as

$$\eta - \eta' = \sum \frac{1}{n!} \frac{d^n \eta}{ds^n},$$

$$\tau - \tau' = \sum \frac{1}{n!} \frac{d^n \tau}{ds^n},$$

$$\phi - \phi' = \sum \frac{1}{n!} \frac{d^n \phi}{ds^n}. \quad (13)$$

Eliminating $s$ from the expressions for $\phi$ and $\tau$ one can obtain the expression for $\phi - \phi'$ as a function of $\tau - \tau'$ with any given precision.

Eq. (1) yields

$$\frac{\partial^{k+l} \Phi}{\partial \eta^k \partial \tau^l} = 0, k = 2m + 1; l, m = 0, 1, 2..., \quad (14)$$

whereas for even $k$ these derivatives are, generally, finite. In this case one of the branches of the zero-field curve (8), (9) corresponds to $\eta = 0$, for the condition (9) is then valid identically.

From eqs. (11), (14) for an arbitrary point of $\eta = 0$ branch of the zero-field curve it follows that $\dot{\eta} = 0$. On differentiating eq. (11) by $s$ and taking into account eq. (14) and $\dot{\eta} = 0$ we find that $\ddot{\eta}$ is also equal to zero. Further differentiations show that in an arbitrary point of the $\eta = 0$ branch of the zero-field curve where $\Phi_{\eta \eta}(0, \tau T_c) \neq 0$ the derivatives of $\eta$ of any order are equal to zero. This is the mere consequence of the fact that the branch under consideration lies on a plane $(\tau, \phi)$ in the space $(\eta, \tau, \phi)$.

And only in the point where

$$\Phi_{\eta \eta}(0, T_c) = 0 \quad (15)$$
there can be a solution $\dot{\eta} \neq 0$ that corresponds to branches $\eta = \eta_\star \neq 0$ of the zero-field curve \(^3\). Therefore, eq. (15) determines the branch point of the zero-field curve. We shall consider the vicinity of this point. All derivatives of $\Phi(\eta, \tau T_c)$ shall be considered as taken in the point $\eta = 0, \tau = 1$.

In the case when eq. (14),(15) are valid eq. (11) becomes an identity. Therefore, in order to calculate $\dot{\eta}, \dot{\tau}, \dot{\phi}$ we must differentiate eqs. (10),(11),(12) one more time:

\[
\begin{align*}
\Phi_{\eta\eta}\ddot{\eta}^2 + 2\Phi_{\eta\tau}\dot{\eta}\dot{\tau} + \Phi_{\eta\tau}\ddot{\tau}^2 + \Phi_{\eta}\ddot{\eta} + \Phi_{\tau}\ddot{\tau} &= \ddot{\phi}, \\
\Phi_{\eta\eta\eta}\dddot{\eta}^2 + 2\Phi_{\eta\eta\tau}\dot{\eta}\dddot{\tau} + \Phi_{\eta\tau}\dddot{\tau}^2 + \Phi_{\eta\eta}\dddot{\eta} + \Phi_{\eta\tau}\dddot{\tau} &= 0, \\
\dddot{\phi} - \Phi_{\tau}\dddot{\tau} &= 0.
\end{align*}
\]

Eqs. (10),(11),(12),(16),(17),(18) yield two solutions:

\[
\begin{align*}
\dot{\eta}_0 &= 0, \ddot{\eta}_0 = \pm\frac{1}{\sqrt{1 + \Phi^2_{\tau}}}, \dot{\phi}_0 = \Phi_{\tau}\dddot{\eta}_0, \\
\dddot{\tau}_0 &= -\frac{\Phi_{\eta}\Phi_{\tau\tau}}{(1 + \Phi^2_{\tau})^2}, \dddot{\phi}_0 = \Phi_{\tau}\dddot{\tau}_0 + \Phi_{\tau\tau}\dddot{\tau}^2_{0},
\end{align*}
\]

and

\[
\begin{align*}
\dot{\eta}_\star &= \pm 1, \ddot{\eta}_\star = \dot{\phi}_\star = \dddot{\eta}_\star = 0, \dddot{\phi}_\star = \Phi_{\tau}\dddot{\eta}_\star.
\end{align*}
\]

Solutions (19), (20) correspond to the branch $\eta = 0$ and branches $\eta_\star \neq 0$ respectively . Here and thereafter subscripts 0 and $\star$ denote that values are taken on and derivatives are taken along the branch $\eta = 0$ and branches $\eta_\star \neq 0$ respectively.

2.1 Critical behavior for $\tau > 1$

In order to obtain critical indexes let us differentiate eqs. (16), (17) and (18) one more time. Taking into account eqs. (14), (15) and (19) we obtain:

\[
\begin{align*}
\phi^{(3)}_0 &= \Phi_{\tau}\dddot{\tau}^{(3)}_0 + 3\Phi_{\tau\tau}\dddot{\tau}_0\dddot{\tau}^2_0 + \Phi_{\tau\tau\tau}\dddot{\tau}^3_0.
\end{align*}
\]

\(^3\) If the functional form of $\Phi(\eta, \tau T_c)$ is known then eq. (15) can be used to calculate $T_c$. 

6
\[ \ddot{\tau}_0 \dot{\phi}_0 (3) + \dot{\phi}_0 \ddot{\phi}_0 (3) + \dddot{\phi}_0 = 0, \]  
\[ \Phi_{\eta\eta} \dot{\tau} \dot{\eta}_0 = 0, \] 
(22)  
(23) 

where superscripts \( (n) \) denote \( n \)th derivatives with respect to \( s \).

Eq. (23) yields \( \dddot{\eta}_0 = 0 \), which is, as we already discussed, a simple consequence that on the branch under consideration \( \eta \equiv 0 \).

The expansion series (13) for the variables \( \phi \) and \( \tau \) up to the terms \( \propto s^3 \) are given by

\[
\tau - 1 = \tau_0 s + \frac{1}{2} \ddot{\tau}_0 s^2 + \frac{1}{6} \tau_0^{(3)} s^3, 
\]
(24)

\[
(\tau - 1)^2 = \tau_0^2 s^2 + \tau_0 \ddot{\tau}_0 s^3, 
\]
(25)

\[
(\tau - 1)^3 = \tau_0^{(3)} s^3, 
\]
(26)

\[
\phi - \phi_0 = \phi_0 s + \frac{1}{2} \phi_0 \dot{s}^2 + \frac{1}{6} \phi_0^{(3)} s^3, 
\]
(27)

where \( \phi_0 = \Phi(0, T_c) \).

Substituting into eq. (27) the expressions (19) and (22) for the derivatives of \( \phi \) and taking into account eq. (26) we obtain

\[
\phi - \phi_0 = \Phi_\tau (\tau - 1) + \frac{1}{2} \Phi_{\tau\tau} (\tau - 1)^2 + \frac{1}{6} \Phi_{\tau\tau\tau} (\tau - 1)^3, 
\]
(28)

which is exactly the same as if one wrote the expansion series for \( \Phi(\eta \equiv 0, \tau T_c) \) in the vicinity of \( \tau = 1 \).

Eq. (28) yields

\[
\left( \frac{d^2 \phi}{d\tau^2} \right)_0 = \Phi_{\tau\tau} + \Phi_{\tau\tau\tau} (\tau - 1). 
\]
(29)

\( \Phi_{\eta\eta}(0, \tau T_c) \) may also be written as an expansion series in \( s \) :

\[
\Phi_{\eta\eta}(0, \tau T_c) = (\Phi_{\eta\eta})_0 s + \frac{1}{2} (\ddot{\Phi}_{\eta\eta})_0 s^2 + \cdots 
\]
(30)

It is easily seen that

\[
(\Phi_{\eta\eta})_0 = \Phi_{\eta\eta} \dot{\tau}_0. 
\]
(31)
Therefore, from eqs. (26), (30) and (31) one obtains

\[ \Phi_{\eta\eta}(0, \tau T_c) = \Phi_{\eta\eta\tau}(\tau - 1). \]  

(32)

If \( \tau \geq 1 \) and \( \eta = 0 \) the conditions \( \Phi_{\eta\eta} \geq 0, C_P > 0 \) must be satisfied. Taking into account eqs. (2), (29) and (32) we find that these conditions demand

\[ \Phi_{\tau\tau} < 0, \Phi_{\eta\eta\tau} > 0. \]  

(33)

From eqs. (2), (29) and (32) also follow the values of the critical indexes:

\[ \alpha_1 = 0, \alpha_2 = -1, \gamma = 1. \]  

(34)

i.e. \( C_P \) and its derivative with respect to temperature are finite in the limit \( T \to T_c + 0 \).

2.2 Critical behavior for \( \tau < 1 \)

On differentiating eqs. (16), (17) and (18) and taking into account eqs. (14), (15) and the solution (20) we obtain

\[ \phi_s^{(3)} = \Phi_{\tau s\tau s}^{(3)}, \]  

\[ \ddot{s}_s = -\Phi_{\eta\eta\eta\eta} (3\Phi_{\eta\eta\tau})^{-1}, \]  

\[ \ddot{\eta}_s \eta_s^{(3)} + \ddot{s}_s^2 (1 + \Phi_s^2) = 0. \]  

(35)

(36)

(37)

The condition \( \tau < 1 \) requires that \( \ddot{s}_s < 0 \). According to eqs. (33) and (36) this is possible if

\[ \Phi_{\eta\eta\eta\eta} > 0, \]  

(38)

i.e. \( \Phi(\eta, \tau T_c) \) as a function of the order parameter \( \eta \) has a minimum in the critical point.

According to eqs. (20) and (37) on the branch \( \eta_s > 0, \dot{\eta}_s = 1 \) the derivative \( \eta^{(3)} \) is negative, whereas on the branch \( \eta_s < 0, \dot{\eta}_s = -1 \) it is positive.

Second differentiation of eqs. (16), (17) and (18) yields
where eqs. (14), (15), (20), (35) and (36) are taken into account.

Third differentiation of eqs. (16), (17) and (18) completes the system of equations necessary to calculate the derivatives $\tau^{(4)}$, $\phi^{(4)}$, and $\eta^{(5)}$.

Further differentiating of eqs. (16), (17) and (18) reveals that on the branches $\eta_* \neq 0$ even derivatives of $\tau$, $\phi$ and odd derivatives of $\eta$ are finite. Different branches $\eta_* > 0$ and $\eta_* < 0$ correspond to different signs of $\eta^{(2n+1)}$.

Fourth differentiation of eq. (16) yields

$$
\dot{\phi}^{(6)}_* = 
\Phi_{\tau} \tau^{(6)}_* + 15 (\Phi_{\tau\tau} \tau^{(4)}_* + \Phi_{\eta\tau} \eta^{(4)}_* + \Phi_{\eta\eta\tau} \eta^{(4)}_*) 
+ 15 \Phi_{\tau\tau\tau} \tau^{(4)}_* + 45 \Phi_{\eta\tau}^{(2,2)} \tau^{(4)}_* + 15 \Phi_{\eta\eta}^{(4,1)} \tau^{(4)}_* + \Phi_{\eta\tau}^{(6,0)},
$$

where we introduced the notation

$$
\Phi_{\eta\tau}^{(n,m)} = \frac{\partial^n+m \Phi}{\partial \eta^n \partial \tau^m}.
$$

Expansion series (13) on the branches $\eta_* \neq 0$ can be written as

$$
\eta = \pm s,
\tau - 1 = \frac{1}{2!} \ddot{\tau}_* s^2 + \frac{1}{4!} \tau^{(4)}_* s^4 + \frac{1}{6!} \tau^{(6)}_* s^6,
\phi - 1 = \frac{1}{2!} \ddot{\phi}_* s^2 + \frac{1}{4!} \phi^{(4)}_* s^4 + \frac{1}{6!} \phi^{(6)}_* s^6,
$$

Eq. (43) gives for up to $s^6$

$$
(\tau - 1)^2 = \frac{1}{4} \dddot{\tau}_* s^4 + \frac{1}{24} \tau^{(4)}_* s^6,
(\tau - 1)^3 = \frac{1}{8} \dddot{\tau}_* s^6.
$$

On eliminating parameter $s$ from the series (44) using expressions (46) we finally obtain
\[ \phi - \phi_0 = \Phi_{\tau}(\tau - 1) + \frac{1}{2} \left( \Phi_{\tau\tau} - 3\Phi_{\eta\eta}^{2} \Phi_{\eta\eta\eta}^{-1} \right)(\tau - 1)^2 + \frac{1}{6} \Phi_{\tau\tau\tau}(\tau - 1)^3, \]  

where

\[ \tilde{\Phi}_{\tau\tau\tau} = \Phi_{\tau\tau\tau} + 3\Phi_{\eta\eta}^{(2,2)} \dot{\eta}_s^{-1} + \Phi_{\eta\eta}^{(4,1)} \ddot{\eta}_s^{-2} + \frac{1}{15} \Phi_{\eta\eta}^{(6,0)} \dddot{\eta}_s^{-3}. \]  

Hence,

\[ \left( \frac{d^2 \phi}{d\tau^2} \right)_* = \Phi_{\tau\tau} - 3\Phi_{\eta\eta}^{2} \Phi_{\eta\eta\eta}^{-1} + \tilde{\Phi}_{\tau\tau\tau}(\tau - 1). \]  

Comparing the expressions (29) and (49) and taking into account inequalities (33) and (33) we obtain

\[ \left( \frac{d^2 \phi}{d\tau^2} \right)_* < \left( \frac{d^2 \phi}{d\tau^2} \right)_0 < 0, \]  

i.e., if the temperature decreases \( C_P \) undergoes finite positive jump in the critical point.

From eqs. (42) and (43) it follows that

\[ |\eta_*| \propto (1 - \tau)^{\frac{1}{2}}. \]  

Expansion series (30) remains valid for the branches \( \eta_* \neq 0 \). Therefore, according to eqs. (14), (20) and (36)

\[ \left( \frac{d\Phi_{\eta\eta}}{ds} \right)_* = \Phi_{\eta\eta\eta} \dot{\eta}_s + \Phi_{\eta\eta\tau} \ddot{\eta}_s = 0, \]  

\[ \left( \frac{d^2\Phi_{\eta\eta}}{ds^2} \right)_* = \Phi_{\eta\eta\eta\eta} \dot{\eta}_s^2 + \Phi_{\eta\eta\tau\tau} \ddot{\eta}_s = -2\Phi_{\eta\eta\tau} \dddot{\eta}_s. \]  

Thus,

\[ \Phi_{\eta\eta}(\eta_*, \tau T_c) = -\Phi_{\eta\eta\tau} \dddot{\eta}_s s^2. \]
And, finally, from (33) and (43) we obtain
\[
\Phi_{\eta}(\eta, \tau T_c) = 2\Phi_{\eta\eta}(1 - \tau) > 0. \tag{54}
\]

Comparing expressions (3), (49), (51) and (54) one readily obtains the values of the critical indexes:
\[
\alpha_1' = 0, \alpha_2' = -1, \beta = \frac{1}{2}, \gamma' = 1. \tag{55}
\]

2.3 Critical behavior in the presence of the external field, \(\tau = 1\)

Consider the proprieties of the system on the line \(\tau = 1\). If the conditions (14), (15) and (38) are satisfied the expansion series of \(\phi\) as a function of \(\eta\) is simply
\[
\phi - \phi_0 = \frac{1}{4!}\Phi_{\eta\eta\eta\eta}\eta^4 + \frac{1}{6!}\Phi_{\eta^6,0}\eta^6. \tag{56}
\]
Second term can be neglected near the first one. According to (4) we then obtain \(\delta = 3\).

In order to determine the critical index \(\epsilon\) it is necessary to calculate second derivative of \(\phi\) with respect to \(\tau\) along the line of a finite external field
\[
h = \Phi_{\eta}(\eta, \tau T_c) = \text{const} \neq 0. \tag{57}
\]
In this case the second term in the right hand side of eq. (5) is not identically zero and we need the expression for the second derivative of \(\eta\) with respect to \(\tau\) along the line (57). On differentiating twice eq. (57) we obtain
\[
\Phi_{\eta\tau} + \Phi_{\eta\eta} \left(\frac{d\eta}{d\tau}\right)_h = 0, \tag{58}
\]
\[
\Phi_{\eta\eta\tau} + 2\Phi_{\eta\eta\tau} \left(\frac{d\eta}{d\tau}\right)_h + \Phi_{\eta\eta\eta} \left(\frac{d\eta}{d\tau}\right)^2_h + \Phi_{\eta\eta} \left(\frac{d^2\eta}{d\tau^2}\right)_h = 0,
\]
where partial derivatives are taken along the line (57) of the surface (8).

Substituting obtained from eqs. (58) expressions for the derivatives of \(\eta\) into eq. (5) we obtain
\[
\left( \frac{d^2 \phi}{d \tau^2} \right)_h = \Phi_{\tau \tau} - \Phi_{\eta \tau} \Phi_{\eta \eta}^{-1} - \Phi_{\eta} \left( \Phi_{\eta \tau} \Phi_{\eta \eta}^{-1} - 2 \Phi_{\eta \tau} \Phi_{\eta \eta} \Phi_{\eta \eta}^{-2} + \Phi_{\eta \tau} \Phi_{\eta \eta} \Phi_{\eta \eta}^{-3} \right).
\]

Expression (60) is obtained for an arbitrary point of the surface (8). It is valid indeed for the line \(\tau = 1\) of this surface. In the vicinity of the critical point the derivatives of \(\Phi(\eta, \tau T_c)\) can be expressed as the expansion series in \(\eta\). Taking into account (14), (15) and (38) we obtain

\[
\begin{align*}
\Phi_{\tau \tau}(\eta, T_c) &= \Phi_{\tau \tau}^0(\eta, T_c) = \Phi_{\eta \tau}(\eta, T_c) = \Phi_{\eta \eta}(\eta, T_c), \\
\Phi_{\eta \tau}(\eta, T_c) &= \Phi_{\eta \tau}^{(2, 2)}(\eta, T_c) = \Phi_{\eta \eta}(\eta, T_c) = \Phi_{\eta \eta}(\eta, T_c), \\
\Phi_{\eta}(\eta, T_c) &= \frac{1}{2} \Phi_{\eta \eta \eta}(\eta, T_c) = \Phi_{\eta \eta}(\eta, T_c) = \frac{1}{6} \Phi_{\eta \eta \eta}(\eta, T_c),
\end{align*}
\]

where the derivatives in the right hand side are taken at \(\eta = 0, \tau = 1\).

Substituting expressions (60) into eq. (60) we can verify that the right hand side of eq. (60) in the limit \(\eta \to 0\) is finite. According to (4) this case corresponds to \(\delta \epsilon = 0\). Therefore,

\[
\delta = 3, \epsilon = 0.
\]

Obtained critical indexes (34), (55) and (61) coincide with ones obtained in the frameworks of the Landau theory [1] except the calculation of \(\alpha_2\) and \(\alpha_2'\). This can be explained by the fact that here we considered by a different approach essentially the same situation as in [1], namely, the problem under constraints (14), (15) and (38).

### 2.4 Tricritical point

Let us consider the situation when beside eq. (15) the following conditions are satisfied:

\[
\Phi_{\eta \eta \eta \eta} = 0, \Phi_{\eta \tau}^{(6, 0)} > 0.
\]

The derivatives (62) do not give any contribution into eqs. (22), (23), (26), (27), (28), (29), (30), (31), (32) and (33). Therefore, the critical behavior on the branch \(\eta = 0, \tau \geq 1\) remains unchanged and the values of critical indexes are given by (34). The critical behavior of the branches \(\eta_* \neq 0\), however, is completely different.
According to eqs. (20), (36), (37), (39) and (62) in this case

\[ \ddot{\tau}_s = \ddot{\phi}_s = \tau_s^{(3)} = 0, \]
\[ \phi_s^{(4)} = \Phi_{\tau} \tau_s^{(4)}. \]  

(63)  

(64)

In order to calculate fourth derivative of \( \tau \) along the branch \( \eta_s \neq 0 \) it is sufficient to differentiate eq. (17) three times and take into account eqs. (14), (15), (20), (33), (62) and (63). The result is

\[ \tau_s^{(4)} = -\frac{1}{5} \Phi_{\eta \tau}^{(6,0)} \Phi_{\eta \tau}^{-1} \eta \Phi_{\eta \tau}^{-1} < 0. \]  

(65)

Eq. (42) has the form

\[ \phi_s^{(6)} = \Phi_{\tau} \tau_s^{(6)} - 2 \Phi_{\eta \tau}^{(6,0)}. \]  

(66)

According to (63) in the expansion series (43) and (44) the quadratic in \( s \) terms are missing. Therefore, according to (43), (44), (62), (63), (64), (65) and (66) it follows that

\[ \phi - \phi_0 = \Phi_{\tau} (\tau - 1) - \frac{4}{3} D (1 - \tau)^{\frac{3}{2}}, \]  

(67)

where

\[ D = \left( \frac{15}{2} \Phi_{\eta \tau}^{3} \left( \Phi_{\eta \tau}^{(6,0)} \right)^{-1} \right)^{\frac{1}{2}} > 0. \]  

(68)

Thus

\[ \left( \frac{d^2 \phi}{d\tau^2} \right)_s = -D (1 - \tau)^{-\frac{1}{2}} \]  

(69)

From eqs. (42), (43) and (65) we obtain

\[ |\eta_s| \propto (1 - \tau)^{\frac{1}{4}}. \]  

(70)

According to (52), (62) and (63) first and second derivatives of \( \Phi_{\eta \eta} \) along the branch \( \eta_s \neq 0 \) are equal to zero in the tricritical point. On differentiating \( \Phi_{\eta \eta} \) third and fourth time and taking into account (14), (15), (20), (62), (63) and (65) we obtain:
\[
\left( \frac{d^3 \Phi_{\eta \eta}}{ds^3} \right)_* = 0 ,
\]
\[
\left( \frac{d^4 \Phi_{\eta \eta}}{ds^4} \right)_* = \Phi_{\eta \eta \tau \tau}^{(4)}* = -4 \Phi_{\eta \eta \tau \tau}^{(4)} .
\]

Therefore, the expansion series for $\Phi_{\eta \eta}$ along the branch $\eta_* \neq 0$ is given by
\[
\Phi_{\eta \eta}(\eta_*, \tau T_c) = \frac{1}{3!} \Phi_{\eta \eta \tau \tau}^{(4)}* s^4 .
\]

Hence,
\[
\Phi_{\eta \eta}(\eta_*, \tau T_c) = 4 \Phi_{\eta \eta \tau \tau}^{(4)} (1 - \tau) > 0 .
\]

According to (14), (15), (56) and (62) on line $\tau = 1$ of the surface (8)
\[
\Phi_{\eta \eta \tau \tau}^{(6,0)}* \eta_*^4 + \Phi_{\eta \eta \tau \tau}^{(4)}* = -4 \Phi_{\eta \eta \tau \tau}^{(4)} .
\]

Therefore, the critical indexes for $\tau \leq 1$ are
\[
\alpha_1' = \frac{1}{2}, \beta = \frac{1}{4}, \gamma' = 1, \delta = 5, \epsilon = \frac{2}{5},
\]

whereas for $\tau > 1$ the indexes are the same as in (34).

Similar consideration can be applied to the case when the first non-vanishing derivative of $\Phi$ with respect to $\eta$ is of order $2k$ ($k$-critical point). In this case the critical indexes for $\tau \leq 1$ are
\[
\alpha_1' = \frac{k - 2}{k - 1}, \beta = \frac{1}{2k - 2}, \gamma' = 1, \delta = 2k - 1, \epsilon = \frac{2k - 4}{2k - 1} .
\]
Fig. 2 represents the sketch of $C_P(T)$ for $k = 2$ and $k > 2$. It is known that neither Fig. 2 nor the critical indexes (34), (77) are in agreement with experimental data. For a majority of real systems $1/3 \leq \beta \leq 1/2, 1 \leq \gamma \leq 4/3, 3 \leq \delta \leq 5$ and $\alpha_1, \alpha_2, \epsilon$ do not deviate significantly from zero. Specific heat $C_P$ anomalously increases as one approaches $T_c$ from above as well as from below.

This character of phase transitions in real systems is usually attributed to non-analyticity of $\Phi$ in the critical point, particularly, to divergence of partial derivatives of $\Phi$. It it is so then the realistic phenomenological theory in either Landau’s or in proposed here geometrical formulation will be impossible.

There is, however, one reason in favor of an “analytical” approach. According to (15), (20), (62) and (69) on the branch $\eta_* \neq 0$, which approaches the critical point along the normal to the surface $(\phi, \tau)$, the derivative $$(d^2\phi/d\tau^2)_*$ may increase infinitely even if the partial derivatives of $\Phi$ with respect to $\eta$ and $\tau$ remain finite. In order that such anomalous increase of $d^2\phi/d\tau^2$ be possible on the branch $\eta = 0, \tau \to 1 + 0$ it is necessary to “take this branch out” of the surface $(\phi, \tau)$ and make it a spatial curve. The feasible approach to this problem is to take into account the dependency of the thermodynamic potential on additional internal parameters characterizing the configuration of the system undergoing phase transition. Contrary to the order parameter $\eta$ these additional parameters must essentially depend on the temperature above as well as below $T_c$.

3 Dependency of the thermodynamic potential on generalized correlation parameters

A system undergoing phase transition is characterized by far as well as near (local) order [3,4]. The far order vanishes above the critical point, whereas correlations describing the local order are finite and essentially depend on temperature both above and below the critical point.

Attempts to create a consistent statistical theory allowing to take into account correlations meet with obstacles of computational as well as theoretical character. Contrary to this, a phenomenological approach avoids the explicit choice of correlation parameters and the calculation of the thermodynamic potential. For the phenomenological approach proposed in this section it is important only that the number of distinguishable configurations of the system is limited and they can be characterized by a limited number of correlation parameters $\lambda_i, i = 0, ..., N - 1$.

Let the function $\Phi(\eta, \lambda_i, T, P)$ defines the dependency of the thermodynamic
potential on the degree of the far order $\eta$, correlation parameters $\lambda_i$, temperature $T$ and pressure $P$. Then

$$\phi = \Phi(\eta, \lambda_i, T, P) \quad (78)$$

defines a hypersurface in the $N + 4$-dimensional space $(\eta, \lambda_i, T, P, \phi)$. Equilibrium states of the system for given $\eta, T, P$ are the points of the hypersurface where

$$\frac{\partial \Phi}{\partial \lambda_i} = 0. \quad (79)$$

and the matrix

$$A_0 = \left| \frac{\partial^2 \Phi}{\partial \lambda_i \partial \lambda_j} \right| \quad (80)$$

is positively determined.

The zero-field line on the surface (78) is defined by the conditions

$$\frac{\partial \Phi}{\partial \eta} = 0, \frac{\partial \Phi}{\partial \lambda_i} = 0 \quad (81)$$

and matrix

$$A_1 = \left| \begin{array}{cccccc}
\frac{\partial^2 \Phi}{\partial \eta^2} & \frac{\partial^2 \Phi}{\partial \eta \partial \lambda_0} & \frac{\partial^2 \Phi}{\partial \eta \partial \lambda_1} & \cdots \\
\frac{\partial^2 \Phi}{\partial \lambda_0 \partial \eta} & \frac{\partial^2 \Phi}{\partial \lambda_0^2} & \frac{\partial^2 \Phi}{\partial \lambda_0 \lambda_1} & \cdots \\
\frac{\partial^2 \Phi}{\partial \lambda_1 \partial \eta} & \frac{\partial^2 \Phi}{\partial \lambda_1 \lambda_0} & \frac{\partial^2 \Phi}{\partial \lambda_1^2} & \cdots \\
\vdots & \vdots & \vdots & \ddots
\end{array} \right| \quad (82)$$

is positively determined.

Let us differentiate $\Phi(\eta, \lambda_i, T, P)$ on $T$ at $P = \text{const}, \eta = \text{const}$:

$$\left( \frac{\partial \Phi}{\partial T} \right)_{\eta, P} = \frac{\partial \Phi}{\partial T} + \frac{\partial \Phi}{\partial \lambda_i} \left( \frac{d \lambda_i}{d T} \right)_{P}. \quad (83)$$

In eq. (83) and thereafter the summation over the repeated index is assumed.

The derivative in the left hand side of eq. (83) is the entropy of the system (up to the sign of the expression). Owing to (79) for equilibrium states of the
system $S = -\partial \Phi / \partial T$. Let $\lambda_i$ be a full set of correlation parameters in the sense that $\eta$ and $\lambda_i$ give the complete description of the configuration of the system. In this case $S$ and $\partial \Phi / \partial T$ are functions of $\eta$ and $\lambda_i$ only and do not depend explicitly on $T$.

On differentiating eqs. (79) and (83) with respect to $T$ we find:

$$
\left( \frac{\partial^2 \Phi}{\partial T^2} \right)_{\eta,P} = \frac{\partial^2 \Phi}{\partial T^2} + 2 \frac{\partial^2 \Phi}{\partial T \partial \lambda_i} \left( \frac{d\lambda_i}{dT} \right)_P + \frac{\partial^2 \Phi}{\partial \lambda_i \partial \lambda_j} \left( \frac{d\lambda_i}{dT} \right)_P \left( \frac{d\lambda_j}{dT} \right)_P,
$$

(84)

$$
\frac{\partial^2 \Phi}{\partial T \partial \lambda_i} + \frac{\partial^2 \Phi}{\partial \lambda_i \partial \lambda_j} \left( \frac{d\lambda_i}{dT} \right)_P = 0.
$$

(85)

Eqs. (84) and (85) yield

$$
\left( \frac{\partial^2 \Phi}{\partial T^2} \right)_{\eta,P} = \frac{\partial^2 \Phi}{\partial T^2} - \frac{\partial^2 \Phi}{\partial \lambda_i \partial \lambda_j} \left( \frac{d\lambda_i}{dT} \right)_P \left( \frac{d\lambda_j}{dT} \right)_P.
$$

(86)

Since $S$ does not depend explicitly on $T$ the first term in eq. (86) is zero. The second term is negative because the matrix (80) is positively determined. By definition, the derivative in the left hand side of eq. (86) in the case of ferromagnets is (for up to the factor $-T$) the specific heat $C_M$, i.e. the specific heat at constant magnetic moment $M = M_0$ and pressure $P$. Therefore, $C_M > 0$.

Eliminating from eqs. (84) and (85) derivatives $(d\lambda_i/dT)_{\eta,P}$ we find:

$$
\left( \frac{\partial^2 \Phi}{\partial T^2} \right)_{\eta,P} = \frac{\det A_2}{\det A_0},
$$

(87)

where the expression for $A_2$ can be obtained from (82) by replacing $\eta \rightarrow T$.

Similarly, the following expression is also obtained:

$$
\left( \frac{\partial^2 \Phi}{\partial \eta^2} \right)_{T,P} = \frac{\det A_1}{\det A_0}
$$

(88)

In order to determine the derivative $(\partial^2 \Phi / \partial T^2)_P$ along the line of zero field on the surface (78) it is necessary to differentiate $\Phi(\eta, \lambda_i, T, P)$ twice by $T$ taking into account the dependency of $\eta$ and $\lambda_i$ on $T$. Eliminating from obtained expressions $(d\lambda_i/dT)_P$ we come up to the equation

$$
\left( \frac{\partial^2 \Phi}{\partial T^2} \right)_P = \left( \frac{\partial^2 \Phi}{\partial T^2} \right)_{\eta,P} - \left( \frac{\partial^2 \Phi}{\partial \eta^2} \right)_{T,P} \left( \frac{d\eta}{dT} \right)_P^2.
$$

(89)
Derivatives (87) and (88) remain finite in the critical point of the surface (78) if the matrix $A_0$ remain positively determined. According to Krivoglaz [6] in this case the values of critical indexes are the same as in the Landau theory, namely, (34) and (77).

Before we shall discuss the situation when $\text{det } A_0 = 0$ in the critical point, let us note that $A_0$ is real and symmetric. Therefore, it is always possible to find a diagonal representation of this matrix by an appropriate choice of $\lambda_i$. Let then in the critical point

$$\frac{\partial^2 \Phi}{\partial \lambda_i \partial \lambda_j} = \delta_{ij} \frac{\partial^2 \Phi}{\partial \lambda_i^2}. \quad (90)$$

Then, taking into account $\partial^2 \Phi / \partial T^2 = 0$, from eq. (86) we obtain

$$\left( \frac{\partial^2 \Phi}{\partial T^2} \right)_{\eta, P} = - \frac{\partial^2 \Phi}{\partial \lambda_i^2} \left( \frac{d\lambda_i}{dT} \right)_P^2. \quad (91)$$

Let us assume that in the critical point

$$\frac{\partial^2 \Phi}{\partial \lambda_0^2} = 0, \quad \frac{\partial^2 \Phi}{\partial \lambda_i^2} > 0, \quad i = 1, 2, \ldots, N - 1. \quad (92)$$

Then, from eq. (85) it follows that if one approaches the critical point the derivative $(d\lambda_0 / dT)_P$ may become infinite while the derivatives of $\lambda_i$ $i = 1, 2, \ldots, N - 1$ remain finite. According to (91) and (92) eq. (89) in the critical point becomes

$$\left( \frac{\partial^2 \Phi}{\partial T^2} \right)_P = \lim_{T \to T_c} \left( \frac{\partial^2 \Phi}{\partial \eta^2} \right)_{T, P} \left( \frac{d\eta}{dT} \right)_P^2 + \frac{\partial^2 \Phi}{\partial \lambda_0^2} \left( \frac{d\lambda_0}{dT} \right)_P^2 - \frac{\partial^2 \Phi}{\partial \lambda_i^2} \left( \frac{d\lambda_i}{dT} \right)_P^2, \quad (i > 0) \quad (93)$$

Thus, it is “critical variables” $\eta$ and $\lambda_0$ which may provide the infiniteness of the derivative (94) and the specific heat $C_P$ in the critical point, whereas the input of other parameters is regular.

On the zero-field line for $T > T_c$ the equilibrium values of $\eta$ and $(d\eta/dT)_P$ are zero identically. Therefore, for $T > T_c$ the first term in (94) is zero. It is
the second term that may lead to anomalous increase of the specific heat at \( T \to T_c + 0 \).

The conditions (90) and (92) greatly reduce the dimensionality of the space where critical behavior is studied. Substituting equilibrium values of “regular” \( \lambda_i(\eta, \lambda_0, \tau T_c), i > 0 \) into eq. (78) one obtains

\[
\phi = \Phi'(\eta, \lambda_0, \tau T_c). \quad (94)
\]

Those points of surface (94) in the four-dimensional space \((\eta, \lambda_0, \tau, \phi)\) for which

\[
\frac{\partial \Phi'}{\partial \eta} = 0, \frac{\partial \Phi'}{\partial \lambda_0} = 0, \frac{\partial^2 \Phi}{\partial \eta^2} > 0,
\]

\[
\frac{\partial^2 \Phi'}{\partial \eta^2} \frac{\partial^2 \Phi'}{\partial \lambda_0^2} - \left( \frac{\partial^2 \Phi'}{\partial \eta \partial \lambda_0} \right)^2 > 0
\]

(95) (96)

constitute the zero-field line.

Since we reduced the set of correlation parameters to one the entropy \( S = -\partial \Phi' / \partial T \) of the system may explicitly depend on \( T \). Because of this, the derivatives of highest than the first order of \( \Phi' \) by \( \tau \) may not be zero.

The critical behavior on the zero-field line and at \( \tau = 1 \) in the vicinity of the critical point will be determined by the order of first non-vanishing derivatives

\[
\frac{\partial^{(2k)} \Phi}{\partial \eta^{(2k)}} > 0, \frac{\partial^{(2n)} \Phi}{\partial \lambda_0^{(2n)}} > 0
\]

(97)

In forthcoming publications we will show the dependency of the critical indexes on the parameters \( k \) and \( n \).

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Fig. 1

$T_a > T_b$
Fig. 2.