The re-examined phenomenological phase transitions theory for ferromagnets

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I. INTRODUCTION

Experimental investigations of the critical phenomena show, that the Landau phase transitions theory does not agree with an experiment. Usually, this fact is attributed to the large fluctuations near the critical point. However the Landau conclusions contradict even the experimental data. In these experiments the temperature dependence of the magnetization near the critical point has been studied. The measurements were carried out by the nuclear magnetic resonance method. In the case of large fluctuations the measurements of the magnetization would be impossible. Therefore, the explanation of discrepancy of the theory and the experiment by very large fluctuations seems to be not convincing enough.

The assumptions which lie in the basis of the Landau theory look natural and simple. That is why we decide to re-analyze carefully this theory. In the process of our analysis we have found one essential circumstance, with which it is necessary to acquaint the reader.

II. THE MODIFICATION OF THE LANDAU THEORY

By examining the symmetry change at the second type phase transitions, Landau presented the crystal density function in the form:

\[ \rho = \sum_{i,n} \eta_i^{(n)} \psi_i^{(n)}. \]  

(1)

Here \( n \) is the index of the irreducible representation of the crystal symmetry group \( G \) in the high symmetry phase and \( \psi_i^{(n)} \) are the basic functions of these irreducible representations.

Denoting by \( \rho_0 \) the invariant at all transformations of the \( G \) group function (this function realizes the unit representation of the \( G \) group), Landau wrote:

\[ \rho = \rho_0 + \delta \rho', \]

(2)

where

\[ \delta \rho' = \sum_{i,n} \eta_i^{(n)} \psi_i^{(n)}, \]

(3)

and the unit representation \( (n = 1) \) is excluded from the summation.

Near the phase transition temperature (critical point \( T_c \)) the expansion of thermodynamic functions in the Landau theory is realized on the powers of small \( \delta \rho' \) with \( \rho_0 \) kept invariable. We suggest that the contribution to the crystal density of the function \( \rho_0 \) can not remain equal to \( \rho_0 (T_c) \) as the temperature changes. Otherwise, far from the critical point, \( \rho_0 (T) \) would be equal to \( \rho_0 (T_c) \), which is obviously not the case.

Instead, it is naturally to present the crystal density \( \rho \) as

\[ \rho = \rho_0 (T_c) + \delta \rho, \]  

(4)

\[ \delta \rho = \delta \rho_0 + \delta \rho', \]  

(5)

\[ \delta \rho_0 = \eta^{(1)} \psi^{(1)}. \]  

(6)

We believe that the expansion of thermodynamic functions on powers of \( \delta \rho \) is mathematically and physically more correct, than the expansion on powers of \( \delta \rho' \). We verify this conjecture in the next Section by calculating the critical index for magnetization and general thermodynamic relations for ferromagnets.

The invariants of the second and higher orders in the expansion of the thermodynamic functions near the critical point correspond to the density change \( \delta \rho_0 \), which does not consist the unit representation. In particular, the second order invariant has the form:

\[ \eta^2 = \sum_i \eta_i^2, \]

(7)

with \( \eta \) being the quantitative measure of the deviation from the critical point.

The linear invariant \( \eta^{(1)} \) corresponds to the density change \( \delta \rho_0 \), which transforms according to the unit representation. This invariant does not determine the symmetry change and does not independent. The magnitudes
\( \delta \rho \) and \( \delta \rho' \) are of the same order. Hence, \( \eta^{(1)} \) is proportional to \( \eta \). This means, that in the expansion of the thermodynamic functions the linear on \( \eta \) term presents. Below we will show for ferromagnets, that keeping the linear term provides the consistency of experiment and theory.

III. THE LINEAR TERM AND THE CRITICAL PHENOMENA IN FERROMAGNETS

Following Landau the linear terms of the thermodynamic potentials expansion are rejected in description of the critical phenomena. One usually uses some additional arguments to exclude the odd terms in the expansion of the ferromagnet’s thermodynamic functions. In the book it is claimed, that the scalar function expansion on the vector quantity may only contain the even power of this quantity. However it is not difficult to show, that this statement is incorrect. Indeed, the first law of thermodynamics for the magnetic systems can be written as

\[
dU = TdS + HdM.
\]

For the Helmholtz potential \( A(T, M) \) we have:

\[
dA = -SdT + HdM.
\]

From the expression it follows that

\[
H = \frac{\partial A}{\partial M} = n \frac{\partial A}{\partial M},
\]

where \( n \) is the unit vector along the \( M \) direction. Thus, we can rewrite Eq. (9) in the following way:

\[
dA = -SdT + HdM.
\]

The example illustrates the general situation that only numerical characteristics of the vectors do appear (via the scalar products) in the expression for the thermodynamic functions. Therefore, it is instructive to expand the ferromagnet’s thermodynamic functions on powers of magnetic moment magnitude. Thus, it is not possible to reject the terms of the expansion with odd powers of the magnetic moment magnitude declaring that the magnetic moment is vector.

In the book the absence of the \( M \) odd powers in the ferromagnet’s thermodynamic functions expansion is justified by the statement, that these functions are even regarding \( M \). However, the change in the \( M \) sign in a ferromagnet is confined to the change of the magnetic field sign (see Eq. (10)). At the simultaneous change of \( M \) and \( H \) signs the thermodynamic functions values do not change. If we expand the thermodynamic function on the magnetic moment magnitude, when \( M \) changes sign, the non-zero coefficients at odd \( M \) powers also change the sign, and the independence of the thermodynamic function on the \( M \) sign will be ensured.

Let us expand the potential \( A(T, M) \) up to fourth power on \( M \) near the critical point:

\[
A(T, M) = \sum_{n=0}^{4} L_n(T)M^n.
\]

For the ferromagnetic phase the equilibrium value of \( M \) is determined from the expression:

\[
H = \left( \frac{\partial A}{\partial M} \right) = L_1(T) + 2L_2(T)M + 3L_3(T)M^2 + 4L_4(T)M^3.
\]

Then consider separately the term \( L_1(T) \) of equation (13). The expansion of \( L_1(T) \) on \( t = T - T_c \) powers up to the first power has the form:

\[
L_1(T) = L_1(T_c) + t \left( \frac{\partial L_1}{\partial T} \right)_{T_c}.
\]

In the ferromagnetic phase \( L_1(T) = 0 \), since at \( T = T_c \) the equilibrium value \( M = 0 \) in the case \( H = 0 \). Hence, the coefficient \( L_1(t) \) is given by

\[
L_1(T) = at,
\]

where

\[
a = \left( \frac{\partial L_1}{\partial T} \right)_{T_c} = \left( \frac{\partial^2 A}{\partial T \partial M} \right)_{T_c} = \left( \frac{\partial H}{\partial T} \right)_{T_c}.
\]

Therefore, the coefficient \( L_1 \) changes the sign at the \( M \) sign change, that is confined with the \( H \) sign change. Thus, the rejection of the linear term of the expansion has no serious theoretical reasons.

Expanding the coefficients \( L \) on powers of \( t \), we rewrite Eq. (13) in the form:

\[
H = \sum_{m,n} a_{mn}t^mM^n.
\]

For the magnetic systems at the phase transition point we have the following relations (in accordance with the general theory of the second-type phase transitions):

\[
\left( \frac{\partial H}{\partial M} \right)_{T_c} = \left( \frac{\partial^2 A}{\partial M^2} \right)_{T_c} = 0,
\]

\[
\left( \frac{\partial^2 H}{\partial M^2} \right)_{T_c} = \left( \frac{\partial^3 A}{\partial M^3} \right)_{T_c} = 0,
\]

\[
\left( \frac{\partial^3 H}{\partial M^3} \right)_{T_c} = \left( \frac{\partial^4 A}{\partial M^4} \right)_{T_c} > 0.
\]

Hence, the terms with \( M \) and \( M^2 \) must be absent in Eq. (17). The terms proportional to \( tM \), \( t^2 \), \( t^2M \), \( tM^2 \) and \( t^3 \) are smaller than the term \( at \), and we may neglect these terms. At the same time we must keep the terms with \( M^3 \), since \( a \) priori the relative values of \( t \) and \( M \).
unknown. As a result, in the case \( H = 0 \) the equation \( \text{[17]} \) takes the form:

\[
H = at + cM^3 = 0, \tag{19}
\]

where

\[
c = \frac{1}{6} \left( \frac{\partial^3 A}{\partial M^3} \right)_{T_c} = \frac{1}{6} \left( \frac{\partial^3 H}{\partial M^3} \right)_{T_c}. \tag{20}
\]

From Eq. (19) we easily find:

\[
M = \left( \frac{-at}{c} \right)^\beta, \quad \beta = \frac{1}{3}. \tag{21}
\]

In the experiments of Heller and Benedek the dependence of \( M^3 \) on \( t \) in MnF\(_2\) in zero external field was studied. This dependence occurs to be linear. Thus, taking into account the linear term in the expansion (12) one achieves the good agreement with the experiments in zero field.

If the odd terms in the expansion (12) are rejected, we return to the Landau-type theory, and get instead of Eq. (13)

\[
H = btM + cM^3 = 0, \tag{22}
\]

where

\[
b = \left( \frac{\partial^3 A}{\partial M^2 \partial T} \right)_{T_c} = \left( \frac{\partial^2 H}{\partial M \partial T} \right)_{T_c}. \tag{23}
\]

From Eq. (22) it follows:

\[
M = \left( \frac{-bt}{c} \right)^\beta, \quad \beta = \frac{1}{2}, \tag{24}
\]

which contradicts with experiments. Moreover, in the Landau-type theory one of the equilibrium values of \( M \) is zero. At the discussion of this fact it is affirmed, that zero solution corresponds to the temperature, which is higher than the Curie point. This statement seems internally inconsistent with physical meaning of the equation (22), for which both zero and non-zero solutions correspond to the same temperature. Alternatively, in our theory the spurious, non-physical solution, \( M = 0 \), does not appear.

It is known, that for magnetic systems the correlation must be fulfilled:

\[
- \left( \frac{\partial M}{\partial T} \right)_H \cdot \left( \frac{\partial H}{\partial M} \right)_T = \left( \frac{\partial H}{\partial T} \right)_M. \tag{25}
\]

Using Eq. (19) and Eq. (21), we find at \( T = T_c \) in correspondence with relation (25):

\[
- \left( \frac{\partial M}{\partial T} \right)_H \cdot \left( \frac{\partial H}{\partial M} \right)_T = a = \left( \frac{\partial H}{\partial T} \right)_M. \tag{26}
\]

If linear term in the expansion is rejected, from Eq. (22) and Eq. (24) at \( T = T_c \) we find:

\[
- \left( \frac{\partial M}{\partial T} \right)_H \cdot \left( \frac{\partial H}{\partial M} \right)_T = t^{\frac{1}{2}} \left( \frac{\partial^2 H}{\partial M \partial T} \right)_T^{\frac{1}{2}} \left[ - \frac{6}{(\partial M/\partial T)^3} \right]^{\frac{1}{2}} = 0. \tag{27}
\]

Hence, the relation (24) does not hold, that is incompatible with thermodynamics of magnetic systems.

In the presence of the external field we rewrite Eq. (17) in the form:

\[
H = at + btM + cM^3. \tag{28}
\]

We retain in the above equation the term proportional to \( tM \), since this term is essential for the explanation of the critical phenomena in the strong magnetic fields.

The dependence of the magnetic moment on the external field near the critical point was studied in the work (26).

In strong magnetic fields the dependence of \( H/M \) on \( M^2 \) occurred to be linear. This result is in agreement with Eq. (28). Indeed, this equation can be converted to the form:

\[
\frac{H}{M} \left( 1 - \frac{at}{H} \right) = bt + cM^2. \tag{29}
\]

In the strong field we can neglect the term \( at/H \) in the left-hand part of Eq. (29) in comparison with unity. As a result we obtain the linear dependence of \( H/M \) on \( M^2 \).

In the Landau-type theory the term \( at/H \) is absent from the very beginning. That is why the experimental results were considered as the confirmation of the Landau-type theory.

With the decrease of the field the domain structure is starting to influence the dependence of \( H/M \) on \( M^2 \). Therefore it is impossible to pick out the contribution of the \( at/H \) term of Eq. (29) to the above experimental results.

We may conclude, that the taking into account the linear term in the expansion of thermodynamic functions is consistent with the experiment both in the strong and zero magnetic fields.

IV. CONCLUSION

We have the serious reasons to consider, that the thermodynamic function expansion up to the fourth power in order parameter is correct at least for the three dimension systems. The origin of the Landau-type theory failures is connected not with the ideological basis of this theory, but with incorrect disregard of the linear term in thermodynamic functions expansion. Keeping of the linear term restores consistency of the theory with an experiment and may promote the better comprehension of phenomena near the critical point.
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