ON THE EXTERNAL FIELD EFFECT IN THE LANDAU THEORY OF THE WEAKLY-FIRST-ORDER PHASE TRANSITION

M.A. Fradkin

Institute of Crystallography, Russian Academy of Sciences

59 Leninsky prospect, Moscow 117333 Russia

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Abstract

The effect of the external field on the weakly-discontinuous first-order phase transition is analyzed in the frame of the Landau theory. The transformation of the free energy expansion as a power series in the order parameter is suggested that maps the first-order phase transition onto the second-order one under the 'effective' external field, that depends on both temperature and on real field value. The presence of the third-degree term in the Ginzburg-Landau expansion is shown to preserve the weakly-discontinuous phase transition for some values of the external field in contrast with the second-order phase transition. The case of proper ferroelastic (martensitic) phase transition from cubic lattice to tetragonal one is considered and the dependence of the transition temperature on the external hydrostatic as well as uniaxial pressure is found.

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It is well-known that the continuous (second-order) phase transition disappears under the applied external field conjugated to the order-parameter. In other word, there is no phase transition when the temperature is varying under the fixed non-zero external field \[1-3\]. For the systems exhibiting weakly-discontinuous first-order phase transition in the absence of the external field, different behavior can occur when the field is applied, because the transition takes place between co-existing phases and sufficiently small field can only change the energy of phases but can not make them unstable. Thus, the field conjugated to the order parameter may shift the temperature of the first-order phase transition instead of suppressing the transition itself.

In the present Letter transformation of the Ginzburg-Landau expansion of free energy as a power series in the single-component order parameter is suggested that maps the first-order phase transition onto the second-order one under the ‘effective’ external field. It is shown that real first-order phase transition is described by the transformed functional, when this ‘effective’ field vanishes. In such a case the transition without the symmetry breaking takes place between two different minima of the free energy, both are corresponding to the low-symmetry phases with different values of the order parameter, so the transitions remains to be of the fist order. The ferroelastic phase transition \[5\] from cubic lattice to tetragonal one provides an example of this situation with respect to spontaneous strain as an order parameter and uniaxial pressure as conjugated external field.

The Landau theory of continuous phase transitions \[1\] suggests that general expression for the (Ginzburg-Landau) expansion of the difference in Gibbs free energy between the phases has the following form

\[
\Delta G = \frac{\alpha}{2} (T - T_c) \eta^2 + \frac{C}{4} \eta^4
\]

where \(T_c\) is a critical temperature and the coefficients \(\alpha\) and \(C\) should be positive. The equilibrium value of the order parameter \(\eta\) is determined by the minimization of \(\Delta G\) with respect to \(\eta\):

\[
\frac{\partial \Delta G}{\partial \eta} = 0 \quad \text{and} \quad \frac{\partial^2 \Delta G}{\partial^2 \eta} > 0.
\]
The solutions are the high-symmetry phase with \( \eta = 0 \), stable for \( T > T_c \) and low-temperature phase with \( \eta^2 = \frac{\alpha}{C}(T_c - T) \) that is stable for \( T < T_c \). The equilibrium phases do not co-exist and the dependence of \( \eta \) on \( T \) is continuous in the critical point, hence this model describes the second-order phase transition.

Upon introducing the effect of external field \( E \), conjugated to the order-parameter \( \eta \), the free energy can be written in the following way

\[
\Delta \tilde{\mathcal{G}} = \frac{\tau}{2} \eta^2 + \frac{\eta^4}{4} - \sigma \eta ,
\]

via convenient units for the field \( \sigma = E/C \), temperature \( \tau = \alpha (T - T_c)/C \) and energy \( \Delta \tilde{\mathcal{G}} = \Delta \mathcal{G}/C \). The condition (2) leads to the cubic equation

\[
\eta^3 + \tau \eta - \sigma = 0
\]

with discriminant

\[
Q = (\frac{\tau}{3})^3 + (\frac{\sigma}{2})^2.
\]

For any value of external field \( \sigma \) the high-symmetry phase with \( \eta = 0 \) no longer provides the stable solution of Eq.(4). Instead, one get \( \eta \neq 0 \) for any temperature.

The cubic equation is known [4] to have one solution in real numbers for \( Q > 0 \) and three ones for \( Q < 0 \). Thus, the additional minimum of the Gibbs free energy appears for

\[
\tau \leq \tau_0 = -3 (\frac{\sigma}{2})^{\frac{2}{3}}.
\]

The \( \Delta \tilde{\mathcal{G}}(\eta) \) curves and the dependencies of \( \eta \) on temperature in different fields are shown in the Fig.1 and Fig.2.

It is seen from the Fig.1 and might be proven rigorously that different minima of the \( \Delta \tilde{\mathcal{G}}(\eta) \) curve have different energies for any temperature \( \tau < \tau_0 \). As the second minimum appears at \( \tau_0 \) with the free energy of \( \frac{3}{4}(\sigma/2)^{\frac{2}{3}} \) which is higher than that of existing high-temperature phase, \(-6(\sigma/2)^{\frac{4}{3}}\), the latter state remains stable throughout all the region of the phase co-existence. Only the condition of \( \sigma = 0 \) through the degeneracy with respect...
to sign of $\eta$ implies the equal energies of different minima and leads to a phase transition of the first order when the external field goes through zero at fixed temperature $\tau < 0$. In other words, the variation of temperature and external field act in a different way on the systems describing by the Ginzburg-Landau expansion (1), because the field variation may lead to the phase change but the temperature one may not.

The weakly-first-order phase transition arises in the Landau theory when the symmetry of the system allows to have third-degree invariant composed by the order-parameter component. Hence, corresponding term should be included in the Ginzburg-Landau expansion:

$$\Delta G = \frac{\alpha}{2} (T - T_c) \eta^2 + \frac{B}{3} \eta^3 + \frac{C}{4} \eta^4.$$  \hspace{1cm} (7)

The physical interest has a case of $B < 0$ and the free energy expansion can be written in the form

$$\Delta \tilde{G} = \frac{C^3}{B^4} \Delta G = \frac{\tau}{2} \zeta^2 - \frac{\zeta^3}{3} + \frac{\zeta^4}{4} - \sigma \zeta ,$$ \hspace{1cm} (8)

with $\tau = \alpha C(T - T_c) / B^2$, $\eta = -(B/C) \zeta$ and $\sigma = -(C^2/B^3) E$.

For the $\sigma = 0$ case, Eq.(2) gives two possible minima of the free energy, those are undistorted phase with $\zeta = 0$ unstable for $\tau < 0$ and low-symmetry one with $\zeta = (1 + \sqrt{1 - 4\tau}) / 2$ appearing for $\tau < 1/4$. Hence, some region of the phase co-existence appears, and the phase energies become equal at $\tau_* = 2/9$, though the supercooling of the high-temperature state as well as superheating of the low-temperature one are possible. The jump in order parameter is $\Delta \zeta = 2/3$ and the nucleation potential barrier has a height $E_b = \Delta \tilde{G}(\zeta_0, \tau_*) = \frac{1}{324}$. It means that the first-order phase transition takes place at the temperature $\tau_*$.  

Substituting $\zeta = \tilde{\zeta} + 1/3$ into the Ginzburg-Landau expansion (8), we get the third-order term excluded

$$\Delta \tilde{G} = \frac{\tilde{\tau}}{2} \tilde{\zeta}^2 + \frac{\tilde{\zeta}^4}{4} - \tilde{\sigma} \tilde{\zeta} + \Delta \tilde{G}_0 ,$$ \hspace{1cm} (9)

where
\[ \tilde{\tau} = \tau - \frac{1}{3}; \quad \tilde{\sigma} = \sigma - \frac{\tau}{3} + \frac{2}{27} \quad \text{and} \quad \Delta \tilde{G}_0 = \frac{\tau}{18} - \frac{\sigma}{3} - \frac{1}{108}. \]

This is equivalent to the free energy expansion (3) for the second-order phase transition under the external field, the only difference consisting of the term \( \Delta \tilde{G}_0 \) that is independent on \( \tilde{\zeta} \). It appears because the free energy is counted with respect to the \((\zeta = 0)\) or \((\tilde{\zeta} = -1/3)\) state, that implies \( \Delta \tilde{G}_0 = \Delta \tilde{G}(\tilde{\zeta} = 0) \neq 0 \).

The condition (3) leads to the cubic equation (4) with the temperature \( \tau \) and field \( \sigma \) replaced by the effective ones \( \tilde{\tau} \) and \( \tilde{\sigma} \), respectively. The sign of discriminant

\[ Q = \left( \frac{\tilde{\tau}}{3} \right)^3 + \left( \frac{\tilde{\sigma}}{2} \right)^2 \propto 4\sigma + 27\sigma^2 - 18\sigma\tau - \tau^2 + 4\tau^3 \]

of this equation indicates, whether it has one root or three ones in the real numbers. The latter case corresponds to the appearance of different minima on \( \Delta \tilde{G}(\tilde{\zeta}) \), second minima of the free energy appearing when \( Q(\tau, \sigma) < 0 \).

Hence, (5) can be considered as the Ginzburg-Landau expansion for the phase transition between the states, related with different minima of the Gibbs free energy. The minima have non-zero values of order parameter, because the symmetry is broken already by the applied field for any temperature. As there is no symmetry breaking, it is not a true phase transition, described by the Landau theory, however, the undistorted phase with \( \zeta = 0 \) can be treated as an analog of ideal high-symmetry "praphase" \( \mathbb{3} \) that would allow the symmetry reduction to both of the phases which provide minima of the free energy.

The phase diagram in \((\tau, \sigma)\) plane is shown at the Fig.3. Additional minimum of the free energy appears for \( \sigma_1 \leq \sigma \leq \sigma_2 \) with

\[ \sigma_{1,2} = -\frac{2}{27} \left( 1 \pm (1 - 3\tau)^{\frac{2}{3}} \right) + \frac{\tau}{3}, \]

that leads to the hysteresis with respect to the external field \( \Delta \sigma = (4(1 - 3\tau)^{\frac{2}{3}})/27. \)

According to an analogy with the second-order phase transition described by (3), the different minima of the \( \Delta \tilde{G}(\tilde{\zeta}) \) have equal energy only at \( \tilde{\sigma} = 0 \). This is the condition of the first-order phase transition and it determines the effect of applied field on transition temperature \( \tau^* \).
\[
\tau_*(\sigma) = 3\sigma + 2/9 .
\] (12)

For \(\sigma = 0\) we get naturally \(\tau_*(0) = 2/9\). The Eq.(12) corresponds to the straight line on \((\tau, \sigma)\) plane (Fig.3). For \(\tau > 1/3\) on this line the equilibrium phase has \(\tilde{\zeta} = 0\) or \(\zeta = 1/3\). This state is an analog of the undistorted high-symmetry phase of the Landau theory without an external field which is unstable for \(\tau < 1/3\). Below \(\tau = 1/3\) on the \(\tau_*(\sigma)\) line it becomes a maximum of \(\Delta \tilde{G}\), located between two minima with \(\tilde{\zeta}_{1,2} = \pm \sqrt{-\tau}\), separated by the energy barrier and the order parameter jump

\[
E_b = \frac{9}{4} \sigma^2 - \frac{\sigma}{6} + \frac{1}{324} \quad \text{and} \quad \Delta \zeta = \frac{2}{3} \sqrt{1 - 2\tau\sigma},
\]

respectively.

As the line of first-order transition in the \((\tau, \sigma)\) phase diagram separates states without symmetry-breaking relation [1], it terminates in critical point \((\tau_c = 1/3, \sigma_c = 1/27)\), which is an analog of the continuous phase transition from the state with \(\tilde{\zeta} = 0\). The jump in order parameter as well as the potential barrier vanish at the critical point, hence, the weakly-first-order phase transition disappears for \(\sigma > \sigma_c\) or \(\tau > \tau_c\). In a contrast with the second-order case where arbitrary small external field destroys the phase transition, here we find that the transition is preserved in the fields lower than \(\sigma_c\).

Let us consider the proper ferroelastic phase transition as an example. The free energy difference between the phases is due to spontaneous strain and can be described by the Ginzburg-Landau expansion of the elastic energy as a power series in the strain components [5,6]. The second-degree term in this expansion is a linear combination of the second-order elastic constants that vanishes at the critical temperature [7]. It is an eigenvalue of the lattice stiffness matrix corresponding to the relevant irreducible representation of the symmetry group of high-temperature phase \(G\) [1] and the strain tensor components transforming with respect to this representation form the order parameter [6]. If the symmetry of low-temperature phase in known \(a\-priory\), than a particular combination of the strain tensor components that is invariant under an action of the symmetry group \(G_1\) of the low-symmetry phase may be treated as a single-component order parameter. Due to long-range
nature of the elastic forces in solids the Landau theory appears to be applicable up to the transition temperature \[3,7\].

In the case of ferroelastic phase transition from cubic to tetragonal lattice the symmetry allows the third-order term to occur in the Ginzburg-Landau expansion, but it appears to be small in In-Tl, \(V_3\)Si and some other alloys \[8\]. Hence, this phase transition should be weakly discontinuous and belongs to the "soft-mode" class, because it is accompanied by a softening of the corresponding acoustic mode of atomic vibrations \[7\]. The Ginzburg-Landau expansion of the elastic free energy up to the fourth order \[9\] is written in terms of a suitable symmetrized combination of the strain components that describes relevant symmetry breaking \[6\]

\[
\eta_1 = (-\epsilon_{xx} - \epsilon_{yy} + 2\epsilon_{zz})/\sqrt{6}
\]  

and corresponds to the extension along \(z\) axis without the volume change. The elastic free energy can be written in the form of Eq.7 with the following elastic constant combinations as coefficients \[9\]

\[
\alpha_1(T - T_c) = (C_{11} - C_{12})
\]

\[
B_1 = (C_{111} - 3C_{112} + 2C_{123})/2\sqrt{6}
\]

\[
C_1 = (C_{1111} - 4C_{1112} + 3C_{1122})/12
\]

There might be an additional degree of freedom that arises from the volume change \[10\]

\[
\eta_0 = (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})/\sqrt{3}
\]  

and contributes the coupling term \(\Delta G_{\text{int}} = D\eta_0\eta_1^2\) with \(D = (C_{111} - C_{123})/(2\sqrt{3})\). This coupling implies the finite volume change at the first-order transition. The minimization of \(\Delta G(\eta_0, \eta_1)\) with respect to \(\eta_0\) leads to renormed coefficients

\[
\alpha = \alpha_1 + 2\alpha_0 D \quad \text{and} \quad C = C_1 - 2D^2/A_0
\]

of the second and fourth orders, with \(\alpha_0\) and \(A_0\) being the volume thermal expansion coefficient and bulk modulus, respectively.
An applied pressure gives rise the 'external' stress tensor $\hat{E}$ corresponding to linear term $-\hat{\epsilon}\hat{E}$ in the elastic energy [12]. The tetragonal symmetry of low temperature phase, determined by the order parameter (13) can only be conserved under $\hat{E}$ having a form

$$E_{i,k} = \delta_{i,k}E_{i,i}; \quad E_{xx} = E_{yy}, \quad (15)$$

of superposition of applied uniaxial pressure along $z$ axis

$$E = (-E_{xx} - E_{yy} + 2E_{zz})/\sqrt{6}$$

with hydrostatic one $P = \text{Tr}(\hat{E})/\sqrt{3}$. Thus, $E$ is the external field, conjugated to the primary order parameter $\eta_1$, whereas hydrostatic pressure is shown [11] to shift the critical temperature of ferroelastic phase transition and, hence, leads to the change of $\tau$ at fixed temperature

$$\tau \rightarrow \tau - \frac{2DC}{A_0B^2} P. \quad (16)$$

The line of the first-order phase transition on the $(T, P, E)$ phase diagram has a form

$$T_*= T_c + \frac{2B^2}{9\alpha C} + \frac{2D}{\alpha A_0} P - \frac{3C}{\alpha B} E \quad (17)$$

with the critical values of temperature $T'_c = T_c + B^2/(3\alpha C)$ and uniaxial pressure $E_c = -B^3/(27C^2)$. The critical hydrostatic pressure depends linearly on the temperature

$$P_c(T) = \frac{A_0}{2D} \left( \alpha(T - T_c) - \frac{B^2}{3C} \right) \quad (18)$$

and vanishes when $T$ goes to $T'_c$.

To conclude, I have considered the transformation of the Ginzburg-Landau expansion of the free energy for the case of the weakly-discontinuous first-order phase transition and have shown that it is equivalent to the free energy expansion for the second-order phase transition with included effect of the external conjugated field. It is shown that in a contrast with the second-order case where arbitrary small external field destroys the phase transition, the first-order transition is preserved in the fields lower than $\sigma_c$. The effect of the external uniaxial
as well as hydrostatic pressure upon the proper ferroelastic (martensitic) phase transition from cubic to tetragonal phase is considered and the equation on the values of the transition temperature, hydrostatic pressure and uniaxial one is derived.

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† Present address: Department of Mechanical and Aerospace Engineering, Carleton University, Ottawa, Ont., K1S 5B6, Canada; e-mail: mfradkin@next.mrco.carleton.ca

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FIG. 1. The dependence of the Gibbs energy on the order parameter $\eta$ under the applied field for different temperatures $\tau_1 > \tau_2 > \tau_0 > \tau_3$ in the case of the second-order phase transition.
FIG. 2. The order parameter dependence on the temperature in various fields for the case of the second-order phase transition. Dashed line corresponds to the absence of external field, $\sigma = 0$. 

\[ \sigma_1 = 0.1 \] 
\[ \sigma_2 = 0.05 \] 
\[ \sigma_3 = 0.01 \]
FIG. 3. The region of the phase coexistence. The dashed line corresponds to points of the first-order phase transition. It terminates in the critical point ($\tau_c = 1/3, \sigma_c = 1/27$).