Intersection of lines of second-order transitions

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(Submitted May 26, 1975
Zh. Eksp. Teor. Fiz. **69**, 1817–1824 (November 1975)

The question of the character of phase diagrams at the intersection of two second-order phase-transition lines is discussed. After an account of the results of the Landau theory, the question of the influence of the critical fluctuations is investigated for this case. The problem of the asymptotic symmetry of the Hamiltonian at the intersection point is solved by Wilson's method. A qualitative investigation of the renormalization-group equations makes it possible to describe the possible types of phase diagrams. The question of the intersection of the superfluid-transition line and the boundary of metastability of solutions of the helium isotopes is also considered.

PACS numbers: 05.70.Fh, 67.20.Qc

1. INTRODUCTION

The temperature of a phase transition depends on different thermodynamic quantities: the pressure, magnetic field, concentrations, etc. Geometrically, we may imagine that the phase transition occurs on a surface in the multi-dimensional space of the thermodynamic variables. Cases in which such surfaces (lines), corresponding to different phase transitions, intersect are possible. In the simplest case of two thermodynamic variables the intersection occurs at a point. For definiteness, in the following we shall speak of phase-transition lines and their point of intersection. Intersections of lines of first-order phase transitions had already been considered by Gibbs. Landau[1] considered the different cases of intersection of lines of phase transitions, in the case when at least one of them is a second-order transition. In this paper we shall be interested in one of the cases considered by Landau—the intersection of two lines of second-order phase transitions. The intersections of lines of ferromagnetic, antiferromagnetic, ferroelectric and different structural transitions in solids can serve as examples. It will be shown that the fluctuation phenomena can substantially alter both the diagram of the state and the character of the critical phenomena. In the last section the closely-related problem of the phase separation of a mixture of the helium isotopes is solved.

2. INTERSECTION OF SECOND-ORDER TRANSITION LINES IN THE LANDAU THEORY

Let φ and ψ be the order parameters associated with two second-order phase transitions. They may be many-component quantities. We shall denote the number of components of φ by n, and the number of components of ψ by m. In the vicinity of the point of intersection of the second-order phase-transition lines the thermodynamic potential can be written in the form of the Landau expansion:

$$\Phi=\Phi_0+\int d^3r\{{}^1/{}_2c[(\nabla\varphi)^2+(\nabla\psi)^2]+\tau(\varphi^2+\psi^2)+\theta(\varphi^2-\psi^2)+{}^1/{}_2[\lambda_1\varphi^4+\lambda_2\psi^4+2\lambda_{12}\varphi^2\psi^2]\}. \quad (1)$$

The number of fourth-order invariants in the Landau expansion may be large. For simplicity, in formula (1) we have written out the terms corresponding to maximum symmetry with respect to rotations of φ and ψ in the n- and m-dimensional spaces. The characteristic feature of the system in the vicinity of the point of intersection of the phase-transition lines is that in the expansion (1) there is a term $\lambda_{12}\varphi^2\psi^2$ describing the interaction between the order parameters φ and ψ.

The quantities τ and θ are linear combinations of the thermodynamic variables, e.g., of the temperature and pressure. For $\tau > |\theta|$ we always have $\varphi = \psi = 0$. The lines $\tau = \pm\theta$ ($\tau > 0$) are the second-order transition lines. Standard thermodynamic analysis of the expression (1) shows that the diagram of the states in the (τ, θ)-plane can be of two types, which are depicted in Fig. 1. In the case when the inequality $\lambda_{12}^2 \geq \lambda_1\lambda_2$ is fulfilled a diagram of the type I is realized. On the line $\tau = +\theta$ ($\tau > 0$) a second-order transition to the phase $\varphi = 0$, $\psi \neq 0$ (the phase ψ) occurs, on the line $\tau = -\theta$ ($\tau > 0$) a second-order transition to the phase $\varphi \neq 0$, $\psi = 0$ (the phase φ) occurs, and on the line

$$(\sqrt{\lambda_2}-\sqrt{\lambda_1})\tau+(\sqrt{\lambda_2}+\sqrt{\lambda_1})\theta=0$$

a first-order transition occurs between these phases.

If $\lambda_{12}^2 < \lambda_1\lambda_2$, a diagram of the type II (Fig. 1b) is realized. On the lines

$$(\lambda_1-\lambda_{12})\tau-(\lambda_{12}+\lambda_1)\theta=0, \qquad (\lambda_1-\lambda_{12})\tau+(\lambda_2+\lambda_{12})\theta=0$$

second-order transitions to a phase with $\varphi \neq \psi \neq 0$ (the phase $\varphi\psi$) occur.

3. INTERACTION OF THE FIELDS FAR FROM THE INTERSECTION POINT

The interaction of the fields φ and ψ turns out to be important not only in the immediate vicinity of the intersection point. We shall consider, e.g., a small region about the line $\tau + \theta = 0$. Near this line the field φ fluctuates strongly, and the fluctuations of the field ψ can be neglected. The strong fluctuations of the field φ can lead to instability with respect to condensation in the field ψ[2]. This means that in the vicinity of the line $\tau + \theta = 0$, where the fluctuations of φ are sufficiently strong, there is a line of first-order phase transitions.

Insofar as the field ψ does not fluctuate, its effect on

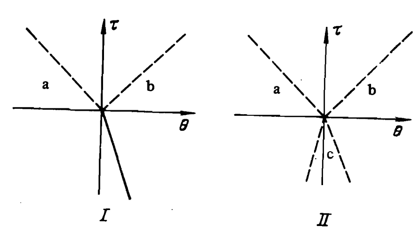

FIG. 1

the field φ can be taken into account by the replacement $\tau + \theta \to \tau + \theta + \lambda_{12}\psi^2$. The singular part Φ_S of the thermodynamic potential of the fluctuating field φ can be written in the form

$$\Phi_s = -\text{const} \cdot |\tau+\theta+\lambda_{12}\psi^2|^{2-\alpha}/\lambda_1. \qquad (2)$$

In order to find the equilibrium value of ψ it is necessary to minimize the thermodynamic potential Φ:

$$\Phi = \Phi_s(\tau+\theta+\lambda_{12}\psi^2) + (\tau-\theta)\psi^2 + \lambda_2\psi^4. \qquad (3)$$

To clarify the physical cause of the instability, we shall estimate the effective coefficient Λ_2 of ψ^4. This coefficient is equal to

$$\Lambda_2 = \lambda_2 + \frac{1}{2}\frac{d^2\Phi_s}{d(\psi^2)^2}\bigg|_{\psi=0} = \lambda_2 - \frac{\lambda_{12}^2}{\lambda_1}C_s(\tau+\theta), \qquad (4)$$

where C_S is the anomalous part of the specific heat. It can be seen from formula (4) that the coupling with the fluctuating field φ leads to an effective attraction for the field ψ.

Investigation of the thermodynamic potential (3) gives the following conditions for the existence of a nonzero ψ:

$$\lambda_{12}^2/\lambda_1\lambda_2 > A, \quad A \sim 1. \qquad (5)$$

In deriving this criterion we have assumed that α is small.

The conditions for the applicability of the theory described are considered in detail in[2] by one of the authors. They have the form

$$T_c^2\lambda_2^2/c^3 < \theta < (\lambda_{12}/\lambda_1)T_c^2\lambda_1^2/c^3. \qquad (6)$$

It can be seen that the conditions (5) and (6) do not contradict each other. It also follows from the inequalities (6) that the instability occurs only on a limited portion of the line $\tau + \theta = 0$.

On decrease of the quantity $\tau + \theta < 0$, the system again falls into the region of applicability of the Landau theory. In this region the phase $\psi = 0$, $\varphi \neq 0$ is realized. Therefore, there exists a second line of first-order phase transitions, delimiting the region $\varphi = 0$, $\psi \neq 0$. A characteristic feature of the transition described is the sharp increase of the susceptibility with respect to φ before the first-order transition with respect to ψ.

4. INTERACTION OF THE FIELDS AT THE INTERSECTION POINT

At the intersection point ($\theta = 0$, $\tau = 0$), both fields, φ and ψ, fluctuate strongly. To construct a theory of such fluctuations we shall use Wilson's ϵ-expansion method[3]. We first consider the problem of the determination of the four-point amplitudes in four-dimensional space. The equations for these amplitudes have the form

$$\begin{aligned} -\dot\Lambda_1 &= 4(n+8)\Lambda_1^2 + 4m\Lambda_{12}^2, & \Lambda_1(0) &= \lambda_1, \\ -\dot\Lambda_2 &= 4(m+8)\Lambda_2^2 + 4n\Lambda_{12}^2, & \Lambda_2(0) &= \lambda_2, \\ -\dot\Lambda_{12} &= 4\Lambda_{12}[(n+2)\Lambda_1 + (m+2)\Lambda_2 + 4\Lambda_{12}], & \Lambda_{12}(0) &= \lambda_{12}. \end{aligned} \qquad (7)$$

Here the dot denotes differentiation with respect to the logarithmic variable $\xi = -\ln(\max\{\tau, \theta, k^2\})$; Λ_1, Λ_2 and Λ_{12} are the renormalized values of the interaction amplitudes[1)].

Equations (7) are homogeneous. It is therefore convenient to change, e.g., to the variables $\Lambda_2 = \Lambda_1 Z$, $\Lambda_{12} = \Lambda_1 U$. Then, for various n and m, we obtain different but topologically equivalent pictures of the phase planes. Such a picture is depicted schematically in Fig. 2. There are five special points. The points 1 and 2 are unstable centers, corresponding to $\Lambda_1 \neq 0$, $\Lambda_2 = 0$, $\Lambda_{12} = 0$ and $\Lambda_1 = 0$, $\Lambda_2 \neq 0$, $\Lambda_{12} = 0$, i.e., corresponding to the symmetries SO(n) and SO(m), respectively. The central point 3 is the stable center. The points 4 and 5 are saddle points. All trajectories that start inside the region bounded by the separatrices (1; 4), (1; 5), (2; 4) and (2; 5) terminate at the center 3.

All trajectories starting outside this region move away to infinity. In these conditions the stability conditions are violated and a first-order phase transition occurs. Depending on the values of n and m, the points 3, 4 and 5 correspond to different symmetries. For $n + m < 4$ the point 3 corresponds to the full symmetry SO(n + m) ($\Lambda_1 = \Lambda_2 = \Lambda_{12}$), the point 4 corresponds to decoupling of the fields, i.e., to SO(n) $\oplus$ SO(m) ($\Lambda_{12} = 0$, $(n + 8)\Lambda_1 = (m + 8)\Lambda_2$), and the point 5 does not correspond to any symmetry higher than the symmetry SO(n) $\times$ SO(m) of the initial Hamiltonian. The separatrix 4-3-5 is determined for $n = m$ by the equality $\Lambda_1 = \Lambda_2$, i.e., corresponds to tetragonal symmetry. The separatrix joining the points 1 and 2 and passing through the point with symmetry SO(n) $\oplus$ SO(m) corresponds to vanishing of the cross-vertex Λ_{12}. On increase of n and m the topological structure of the phase plane remains as before, but, from the point of view of the symmetry, the points 3, 4 and 5 change places. For definiteness, as before we shall denote the stable center by the number 3 and the left and right saddle points by the numbers 4 and 5 respectively. Then, for $n + m > 4$, the point 5 corresponds to the full symmetry SO(m + n). The possible symmetries of the center 3 for $n + m \geq 4$ are as follows ($m \leq n$); for $m = 1$ and $n < 10$, for $m = 2$ and $n < 7$, for $m = 3$ and $n < 6$, and for $n < 4$, the lowest possible symmetry is realized—the symmetry SO(n) $\times$ SO(m); for all other values of n and m ($m \leq n$) the point 3 possesses the symmetry SO(n) $\oplus$ SO(m) ($\Lambda_{12} = 0$, $(n + 8)\Lambda_1 = (m + 8)\Lambda_2$).

The example considered illustrates a general feature arising in the fluctuation theory of phase transitions: the asymptotic symmetry arising on a phase-transition line can turn out to be higher than the symmetry of the initial system. The scale invariance of the fluctuations is, in any case, such a symmetry. As can be seen from, in particular, the example considered, on a phase-transition line the appearance of new rotational symmetries, not possessed by the initial system, is possible. The first example of an asymptotic rotational symmetry was considered by Wilson and Fisher[3].

5. POSSIBLE TYPES OF STATE DIAGRAMS

The form of the state diagram is determined by the following principal factors:

1. The existence of narrow regions ("ears") bounded by two first-order transition lines (cf. Sec. 3). A necessary condition for the existence of ears is that the inequality (5) be fulfilled. To simplify the situation we shall assume that the constant A appearing in it is equal to unity. The condition for the existence of an ear near the phase transition to the phase φ has the form $\lambda_{12} > \lambda_2^2/\lambda_1$, and near a transition to the phase ψ has the same form but with interchange of the indices 1 and 2. In these inequalities we have also put the corresponding constant equal to unity.

2. The form of the state diagram for large negative values of τ. This is determined by the sign of the inequality $\lambda_{12}^2 \gtrless \lambda_1\lambda_2$ (cf. Sec. 2).

3. The form of the phase diagram is also determined by the positions of the bare values λ_1, λ_2 and λ_{12} in the phase plane (Fig. 2). If they lie in the region bounded by the separatrices 1-4, 2-4, 1-5 and 2-5, an intersection of second-order phase-transition curves occurs. But if they lie outside this region, a first-order transition occurs for values of τ still not equal to zero.

Figure 3 depicts half of the phase plane for the case n = m = 1. As the variables we have chosen $x = (\Lambda_1 - \Lambda_2)/(\Lambda_1 + \Lambda_2)$, $y = \Lambda_{12}/(\Lambda_1 + \Lambda_2)$. The regions of instability ($\Lambda_1 < 0$ and $\Lambda_{12} < 0$, $\Lambda_{12}^2 > \Lambda_1\Lambda_2$) are shaded. The dashed-dotted curve is determined by the equation $\Lambda_{12}^2 = \Lambda_1\Lambda_2$ ($\Lambda_{12} > 0$). The dashed lines are determined by the equations $\Lambda_{12} = \Lambda_2^2\Lambda_1^{-1}$ and $\Lambda_{12} = \Lambda_1^2\Lambda_2^{-1}$. The separatrices are plotted as thick solid lines. The thin solid line is the integral curve intersecting the y-axis at a right angle. All the integral curves lying above this curve necessarily intersect the dashed-dotted line $\Lambda_{12}^2 = \Lambda_1\Lambda_2$. The lines enumerated are the boundaries of the regions A, B, C. D, E, F, G and H, as indicated in Fig. 3. The state diagrams shown in Fig. 4 correspond to bare values λ_1, λ_2 and λ_{12} represented by points in one of these regions.

We shall clarify how the line of first-order phase transitions arises in the diagram F. The corresponding integral curve starts in the region F of the phase plane, intersects the dashed-dotted line and falls through the regions E and O into the stable center. On further decrease of τ the point representing the system moves along the same integral curve in the opposite direction. So long as this point is situated in the regions D and E, the inequality $\Lambda_{12}^2 > \Lambda_1\Lambda_2$, corresponding to the phase diagram I in Fig. 1, is fulfilled. On further decrease of τ the representative point intersects the dashed-dotted line and the inequality changes sign; this corresponds to the diagram II in Fig. 1. The final form of the diagram is depicted in Fig. 4.

If the initial value corresponds to a point in the region H, the integral curve intersects the stability boundary while τ is still > 0. A first-order phase transition to the phase $\varphi\psi$ occurs. The phase diagram H for this case is shown in Fig. 4.

Using analogous arguments we can obtain all the other diagrams of Fig. 4. When $n + m \geq 4$, the symmetric point through which the dashed-dotted and dashed lines pass becomes a saddle point. In this case, regions corresponding to the diagrams A, B, C, G and H in Fig. 4 exist, the diagrams D and F are absent, and in place of the diagram E there arises the new diagram depicted in Fig. 5.

6. CURVE OF CRITICAL POINTS IN A SUPERFLUID SOLUTION

The phase diagram of a solution of the helium isotopes shows that, within the experimental errors, the line of λ-transitions passes through the vertex of the phase-separation curve[5]. One of the possible explanations of this fact is that this point is a tricritical point[6], i.e., the coefficients of ψ^2 and ψ^4 in the Landau expansion vanish at this point. For a more detailed investigation of this possibility we shall assume that phase separation of a mixture of He^3 and He^4 would also occur in the absence of the superfluid condensate, on lowering of the temperature. That such an assumption is realistic is indicated by the phase diagram of a mixture of solid helium isotopes[5]. It can be seen from this phase diagram that a mixture of solid isotopes separates and has a critical phase-separation point.

We shall consider this possibility in the framework of the Landau theory. The thermodynamic potential Ω is a function of the temperature T, chemical potential μ, concentration c and pressure p, and can be written in the form

$$\Omega_s = \Omega_n + {}^1/_2\tau(c, p)\psi^2 + {}^1/_4\lambda\psi^4. \tag{8}$$

The subscripts s and n correspond to the superfluid and normal phases. In particular, the potential Ω_n describes the phase separation in the absence of the superfluid condensate. In accordance with the experimental situation, it is assumed that phase separation sets in as the temperature is lowered.

Eliminating ψ by means of the equilibrium equation $\partial\Omega_s/\partial\psi = 0$, we obtain the thermodynamic potential of the superfluid phase in the form

$$\Omega_s = \Omega_n - \tau^2(c, p)/4\lambda. \tag{9}$$

The boundary of the region of stability of the solution is described by the equations $\partial\Omega/\partial c = 0$, $\partial^2\Omega/\partial c^2 = 0$. Using the expression (9), we obtain the equation of the boundary of stability for the superfluid phase:

$$\frac{\partial^2\Omega_s}{\partial c^2} = -\frac{1}{2\lambda}\left(\frac{\partial\tau}{\partial c}\right)^2 + \frac{\partial^2\Omega_n}{\partial c^2} = 0. \tag{10}$$

Since the phase separation sets in on lowering of the temperature, for a fixed concentration the points at which $\partial^2\Omega/\partial c^2 > 0$ correspond to higher temperatures than the corresponding points on the stability boundary ($\partial^2\Omega/\partial c^2 = 0$) of the normal phase. In particular, this means that the stability boundary (10) of the superfluid phase lies higher in temperature than the stability

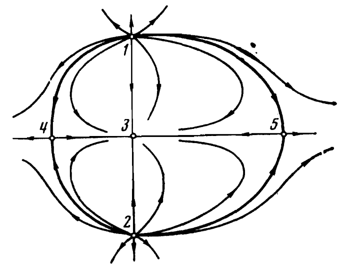

FIG. 2

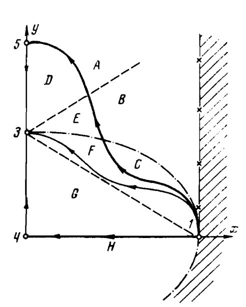

FIG. 3

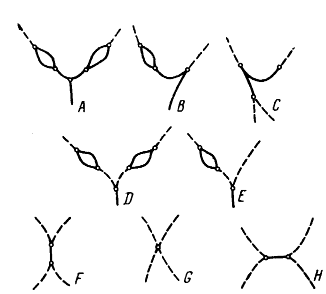

FIG. 4

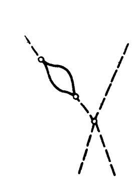
FIG. 5

boundary of the normal phase. At different pressures the line of λ-transitions intersects the phase-separation curve of the normal phase or the stability boundary of the superfluid phase at different points. The possible types of phase diagram are depicted in Fig. 6. In this figure the phase-separation curves are plotted by solid lines and the curves of absolute instability of the superfluid phase by dashed-dotted lines. The equilibrium curves of the normal phase are plotted by a thin dashed line. The lines of λ-transitions are plotted by a thick dashed line. In the case depicted in Fig. 6a, the line of λ-transitions intersects the phase-separation curve of the normal phase before the dashed-dotted line does. This leads to phase separation into superfluid and normal phases. The phase-separation curves at temperatures below the temperature of the point of intersection are slightly distorted.

Another simple possibility is realized if the curve of λ-transitions passes above the critical phase-separation point in the superfluid phase (the point K′). In this case, phase-separation into two superfluid phases occurs near K′. On lowering the temperature the line of λ-transitions may not intersect the phase-separation curve (Fig. 6e). In the case when such an intersection does occur, the solution separates into a superfluid and a normal phase at a temperature below the intersection point.

Figures 6b, 6c and 6d correspond to the case when the λ-transition line intersects the stability boundary of the superfluid solution (the point T_p). On further lowering of the temperature, phase separation into superfluid and normal phases occurs. At the point T_p the concentrations of the separating components are equal. The phase-separation curves $c_1(T)$ and $c_2(T)$ are determined by the equalities

$$\Omega_s(c_1)=\Omega_n(c_2), \quad \left(\frac{\partial\Omega_s}{\partial c}\right)_{c=c_1}=\left(\frac{\partial\Omega_n}{\partial c}\right)_{c=c_2}=0. \tag{11}$$

Assuming c_1 and c_2 to be close, Eqs. (11) can be rewritten in the form

$$\frac{1}{2}\frac{\partial^2\Omega_n}{\partial c^2}(c_1-c_2)^2-\frac{1}{4\lambda}\tau^2=0, \tag{12}$$

$$\frac{\partial^2\Omega_n}{\partial c^2}(c_1-c_2)-\frac{1}{2\lambda}\left(\frac{\partial\tau}{\partial c}\right)\tau=0.$$

The condition for the compatibility of Eqs. (12) has the form

$$\frac{\partial^2\Omega_n}{\partial c^2}=\frac{1}{2\lambda}\left(\frac{\partial\tau}{\partial c}\right)^2 \tag{13}$$

Comparing the expression obtained with formula (10), we can convince ourselves that the point T_p belongs to the stability boundary of the superfluid solution. Using the equalities (12) and (13), we obtain $\tau(c_2) = 0$. This means that the curve $c_2(T)$ and the λ-transition line have a common tangent at the point T_p. In order to obtain the curve $c_1(T)$, it is necessary to keep terms of third order in $c_1 - c_2$. Thus, the superfluid transition greatly changes the phase diagram. In a broad range of pressures, a diagram is realized in which the vertex of the phase-separation curve (the point T_p) lies on the λ-transition line.

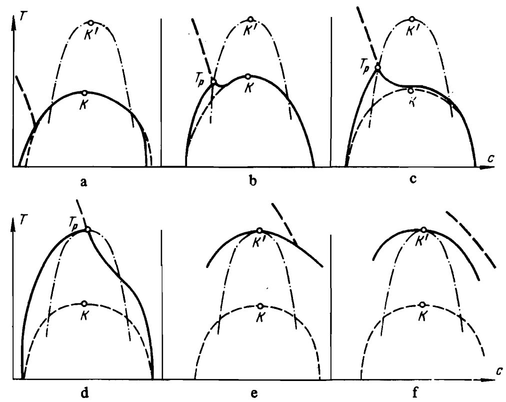

FIG. 6

Elementary calculations show that the points T_p are tricritical in the conventional sense, i.e., in the sense that the coefficients of ψ^2 and ψ^4 in the Landau Hamiltonian vanish at these points. From general arguments it is difficult to say anything definite about the curve $T_p(c)$ of tricritical points corresponding to different pressures. The assumption that a mixture of helium isotopes can also undergo phase separation without the superfluid condensate enables us to assert that the curve $T_p(c)$ has a maximum of the point K′. Therefore, in addition to diagrams with tricritical points, other types of phase diagram are possible. From the point of view of comparison with experiment, the diagram of Fig. 6e is of special interest. In this case the right-hand part of the phase-separation curve does not have a common tangent with the λ-transition line, and the vertex of the phase-separation curve is smooth, without the discontinuity that is characteristic for a tricritical point. Observation of phase separation into two superfluid phases would serve as a proof of the existence of a diagram of the type in Fig. 6e.

[1)]Similar equations for the particular case n = 1 have been investigated in [4] by Nelson, Kosterlitz and Fisher.

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Translated by P. J. Shepherd
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