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## Tricritical Points and Type-Three Phase Transitions\*

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Phase transitions with tricritical points occur in catastrophes generated by sixth-order polynomials. The catastrophe theory of the phase transition is more general than the corresponding Landau theory (at the expense of some of its predictive power) and does not suffer from some of the defects of that theory in its application to systems such as metamagnets, He<sup>3</sup>-He<sup>4</sup> solutions, and ferroelectrics. Some consequences of the use of the polynomial—including cubic terms also—are explored.

### I. INTRODUCTION

“Tricritical points”<sup>1,2</sup> are points in thermodynamic phase space where a phase transition of a complex kind takes place involving the meeting of a line of second-order transitions with a line of first-order transitions. There are indications<sup>1</sup> that the “classical theory,” that is, the Landau theory of phase transitions, is inadequate for the description of this phenomenon. In this paper we show that the Landau theory, as generalized by the theory of catastrophes,<sup>3</sup> in fact, provides a phenomenology of tricritical points. This is because the catastrophe theory based as it is on topological methods confines itself almost entirely to qualitative statements. While this has the weakness of precluding quantitative predictions, it has the advantage that it cannot be contradicted by quantitative results either. In defense of this unusual approach to physical theory, it might be said that the real problem of phase transitions is a qualitative one, namely, to explain the mutual resemblance of phase transitions despite the diversity of the systems in which they appear. (Certain simple assumptions within this theory do lead to definite quantitative results; this is discussed in Sec. II.)

In Ref. 3 is an outline of catastrophe theory. We here repeat only as much as is necessary to introduce notation. For each point  $x$  in an external parameter space  $X$ , a system has available a manifold  $M_x$  of internal states. The internal state  $\bar{m}_x$

which the system actually assumes is that  $m \in M_x$  which minimizes a given potential function  $V_x(m)$ ,  $V_x: M_x \rightarrow R$ . If at some  $x_0$ , the motion at  $\bar{m}_{x_0}$  is not structurally stable, then the Hessian

$$H_{ij} = \left. \frac{\partial^2 V_{x_0}}{\partial \mu_i \partial \mu_j} \right|_{\bar{m}_{x_0}} \quad (1.1)$$

( $\mu_i$  local coordinates on  $M_{x_0}$ ) is not positive definite and there is at least one vector (i.e., direction in  $M_{x_0}$ )  $j$  such that

$$Hj = 0 \quad (1.2)$$

A catastrophe is said to occur at  $x_0$ . Here  $j$  is called the Jacobi field, and the dimension of the space of such vectors is the internal dimension of the catastrophe. Smoothness assumptions are made for  $V_x$ , in particular for its dependence on  $x$ . Since  $V_{x_0}$  is not structurally stable, there are potentials near it (in the topology on the space of potentials, here taken to be a  $C^2$  topology) which are not equivalent to it. “Equivalence” is defined purely topologically:  $V_i: M \rightarrow R$ ,  $i = 1, 2$ ;  $V_1 \sim V_2$  if there exist  $h: M \rightarrow M$ ,  $k: R \rightarrow R$ , homeomorphisms, such that

$$V_1(h(m)) = k(V_2(m)) \quad (1.3)$$

for all  $m \in M$ . If all potentials in a neighborhood of  $V_{x_0}$  are equivalent to some potential of the form

$$V_{x_0} + \sum_{k=1}^N a_k g_k, \quad g_k: M \rightarrow R, \quad (1.4)$$

for varying  $a_k$  and some fixed family of  $g_k$ , then the

catastrophe at  $x_0$  is said to be of finite codimension  $N$ . It can be shown that for catastrophes of finite codimension the functions  $g_k$  can be taken as monomials in local coordinates near  $\bar{m}_{x_0}$ . Thus for a catastrophe of codimension  $N$ , internal dimension 1, each potential near  $V_{x_0}$  is equivalent to

$$V_{x_0} + \sum_{j=1}^N v_j \mu^j \quad (1.5)$$

for some value of the numbers  $v_1, \dots, v_N$ , with  $V_{x_0}$  itself equivalent to  $\mu^{N+2}$ , where  $\mu$  is a coordinate whose axis is a curve tangent to  $j$  at  $\bar{m}_{x_0}$ . Given the smooth dependence of  $V_x$  on  $x$ ,  $V_x$  for  $x$  near  $x_0$  must be equivalent to a potential of the form (1.5) so that up to equivalence

$$V_x = \mu^{N+2} + \sum_{j=1}^N v_j(x) \mu^j. \quad (1.6)$$

It follows that  $v_j(x_0) = 0$ .

In Ref. 3 the following correspondence was made with statistical mechanics:  $X$  is the thermodynamic phase space;  $M_x$  are internal states, specifically assumed to be described by some order parameter so that  $M = \{\text{order parameters}\} = \{\eta\}$ ;  $V_x(m)$  is the free energy at  $x$  for a given order parameter  $m$  (or  $\eta$ ). [A more usual notation for this is  $F_{T\mu V}(\eta)$ ;  $F$  is actually part way between energy and free energy and might be called constrained free energy.] Higher-order phase transitions were related to catastrophes; the Jacobi field  $j$  was identified as a zero-free-energy excitation of the system, and in fact is a nonlocalizable mode of the Goldstone sort, in this case connected with the degeneracy of the equilibrium state below the critical temperature. This is analyzed in Ref. 4. In thermodynamics, absolute minima of  $F$  are desired so that only even  $N$  are acceptable. Let  $T = 1 + \frac{1}{2}N$  and call  $T$  the "type" of the phase transition. It was noted in Ref. 3 that the most common higher-order phase transitions are those of type two; however, type-three transitions were indicated experimentally for certain ferroelectric transitions. It was suggested that the polynomial of the form (1.5) be used to classify phase transitions. For catastrophes of internal dimension 1 these polynomials are characterized by  $N$  or alternatively by the type  $T$ .

It should be noted that while topologically speaking any potential near the catastrophe point is equivalent to the polynomial (1.6) (for some  $\{v_i\}$ ), from a physical point of view this does not mean that  $V(\mu)$  as given by (1.6) is the free energy of the entire system. Rather, once a coordinate  $\mu$  has been picked, the variation of  $\mu$  takes us through only a one-dimensional family of states and hence the polynomial  $V(\mu)$  can be interpreted physically as the free energy of a single "mode." All that the general theory of catastrophes says is that sufficiently close to the catastrophe the potential  $V$  for

any variation other than change of  $\mu$  is stable. [ $V$  is now considered as  $V(m)$ , a function of the many-dimensional order parameter.] The general theory gives no *a priori* estimate of how flat the minima in directions other than the Jacobi field might be beyond the stability of  $V$  in these directions. For thermodynamic systems some of these minima will be very flat indeed<sup>5</sup> and this is why catastrophe theory alone is not adequate for a discussion of heat capacities and susceptibilities. These latter arise from fluctuations in which modes near the Jacobi field play an important role.

In this paper we discuss the proposition that tricritical points are characteristic of phase transitions of type three. For ferroelectrics (and some other substances too) Benguigui<sup>6</sup> has examined the thermodynamic quantities in the neighborhood of the point (in thermodynamic phase space) where the fourth-order term in the expansion of free energy in powers of polarization<sup>7,8</sup> vanishes. This point is the tricritical point. Later in this paper, further examination of the qualitative pattern of states near the tricritical point will be undertaken. First, though, it is necessary to consider the objections raised<sup>1</sup> against the Landau theory as a vehicle for describing this sort of phase transition. Obviously if simple application of Landau theory gives an unrealistic picture of the phase transition, then nothing is gained by manipulating polynomials and getting elaborate predictions on the states of the system near the tricritical point.

Objections to the Landau theory are both experimental and theoretical. Landau theory makes predictions about critical exponents and the slope of certain lines in phase space which are not borne out either in real substances or in models. Furthermore, derivations (including that of Ref. 3) are related to mean-field theory which must break down close enough to a critical point—hence so must Landau theory.

That catastrophic Landau theory makes no predictions about critical exponents—not even that they exist—is the burden of Sec. II. We also address the question of derivation. In Sec. III we study the system's morphology near the tricritical point and discuss certain experiments suggested by the theory.

## II. QUANTITATIVE PHENOMENA NEAR A CATASTROPHE

In the classical theory one assumes a form for the free energy,

$$F = P^6 + \gamma P^4 + \alpha P^2 + EP \quad (2.1)$$

(here looking at the example of a ferroelectric) and takes  $P$  to be an observed quantity such as polarization,  $E$  external electric field, and the other parameters functions of temperature and constituents of the system. Assuming definite depen-

dencies of  $\gamma$  and  $\alpha$  on  $T$ , etc. [e.g.,  $\alpha = (\text{const.}) \times (T - T_c)$ ], values for the critical indices are derived. The index  $\delta$  ( $P \sim E^{1/\delta}$  for  $\gamma = \alpha = 0$ ) depends only on the term  $EP$  and is always 5 for the polynomial (2.1). For type-two transitions, derivations of the critical indices are given by Kadanoff *et al.*<sup>9</sup>; for type three, Benguigui<sup>6</sup> obtains the critical indices and observes too that the slopes of the lines of first- and second-order transitions need not be the same.

Catastrophe theory arrives at a polynomial of the form (2.1) in the following way: A certain pattern of lines and surfaces is observed in thermodynamic phase space. This is identified as being capable of coming from a minimum principle of a sixth-order polynomial whose coefficients are continuous functions in this phase space and whose variable is a *one-dimensional* order parameter. We do not assume that we have a derivation of this minimum principle (although in Ref. 3 we discuss how such a minimum principle could arise from the method of steepest descents for functional integrals). In particular the quantity  $P$  appearing in the polynomial need not be linearly related to the most conveniently observed physical quantity (polarization in this case). The most we can expect—in view of the fact that in catastrophe theory, potentials are defined only up to topological equivalence—is that the variable appearing in the polynomial (2.1) is a *monotonic* function<sup>10</sup> of the usual physical order parameter (polarization, magnetization, etc.).

For example, if it is assumed that a certain phase transition is described by a polynomial

$$V_x(\mu) = \mu^6 + v_4\mu^4 + \dots + v_1\mu, \quad (2.2)$$

then if  $v_4 = v_3 = v_2 = 0$ ,

$$\mu \sim (v_1)^{1/5}, \quad (2.3)$$

which would give  $\delta = 5$  if  $\mu$  were the order parameter and if  $v_1 = E$ . If instead,

$$\mu = f(P), \quad (2.4)$$

where  $P$  is the physical order parameter (say polarization) and  $f$  is monotonic, no conclusions about  $\delta$  can be drawn from (2.3). For example, if

$$f(P) = P^\theta, \quad (2.5)$$

then  $\delta = 5\theta$ . If  $f$  were not a power at all, there would be no critical exponent (and therefore there is certainly no requirement for scaling in this theory).

The transformations ( $f$ ) discussed here may have a large effect on  $V$  in the  $C^2$  topology; however, the definition of equivalence of potentials makes no reference to their smoothness so this is no drawback. This means that if one insists on using certain variables (e.g.,  $P$ ) he may find no polynomial potential; nevertheless, the morphology in phase space indicates that for some variable, bearing a

one-to-one relation to  $P$ , there is a polynomial potential.<sup>11</sup>

The foregoing remarks should make it clear that we advocate catastrophe theory as a kind of phenomenology. For this reason one might go a step further and include (2.5) in his assumptions. Alternatively, one might set  $\theta = 1$  far from the critical point (agreeing with the usual Landau theory), while closer in, dynamical effects might (smoothly) change this to another value. Also various dependencies of  $v_i$  ( $i = 4, 2, 1$ ) on the external variables might be considered. In this way one generates definite predictions (for example, those of Ref. 6) for some of the critical exponents.

Heat capacities are another matter and involve assumptions on the free energy of modes other than that of the Jacobi field. (Heat capacities arise from fluctuations; the contribution of any one mode drops out in the thermodynamic limit.) To the extent that the polynomial (2.2) can be interpreted as a free energy, it is the free energy of only a single mode. This mode, the Jacobi field, is the eigenvector of the Hessian with zero eigenvalue. There will be eigenvectors of nearly zero eigenvalue—very many as a matter of fact—so the question is, what are the nearby states and how fast does the eigenvalue grow? Without these considerations one would get the Landau result that the specific heat is simply discontinuous.<sup>12</sup> Thus, as remarked in Ref. 3, the specific heats involve input beyond the polynomial (2.2) which therefore does not determine them. Again, specific assumptions will yield definite critical exponents.

We find therefore that quantitative objections to the Landau theory do not apply to catastrophe theory: Critical exponents, angles between lines, etc., are simply not part of the predictions of the topological theory. (The *qualitative* predictions of the theory will be considered in Sec. III.)

Landau theory is sometimes related to mean-field theory<sup>13</sup>; similarly, in Ref. 3 the method of steepest descents was used in a demonstration that catastrophes arise in statistical mechanics. It may be more accurate, however, to disown all derivations of catastrophe theory and to emphasize the character of the theory as a framework for phenomenology.

### III. NEIGHBORHOODS OF THE CATASTROPHE

The (constrained) free energy for the Jacobi mode is assumed to be of the form

$$F_x(\mu) = \mu^6 + \sum_{i=1}^4 v_i(x)\mu^i, \quad (3.1)$$

with  $v_i(x_0) = 0$ ,  $i = 1, 2, 3, 4$ ;  $x_0$  is the location of the catastrophe.  $\mu$  is a monotonic function of the order parameter.  $v_i$  are functions of  $T$ , etc., but we here consider them the independent variables

in  $X$  space.

In this section we discuss morphology; what will the system look like in various regions of  $X$ ? Where are the phase transitions (types one and two)? Much of this ground has been covered by Landau<sup>14</sup> and others. We wish to emphasize further developments naturally suggested by the catastrophe theory.

First assume  $v_1 = v_3 = 0$ . In Fig. 1 we map out regions in the  $v_2v_4$  plane and indicate the locations and types of phase transitions.

Of interest here are the regions where three distinct minima exist. The line  $v_4 = -2(v_2)^{1/2}$  is a set of "triple points." To its left is a region where  $\mu = 0$  is a metastable state. (We make the following physical identification: Minima of the constrained free energy which are not absolute minima correspond to metastable states. Nothing in catastrophe theory *per se* either justifies or denies this identification.) Just as is the case for type-two phase transitions on the line of first-order transitions, the system can jump one way or the other—here, however, the process may take a long time and the fluctuations, etc., might be studied [see Fig. 2(f)]. If  $v_2 \rightarrow 0^+$  with  $v_4 < 0$ , the metastable state goes out of existence and the more familiar situation of a first-order transition obtains.

For  $v_1 \neq 0$ ,  $v_3 = 0$ , the  $\mu - \mu$  symmetry is broken. Again some novel situations arise in regions where three distinct minima exist. The linear term can be used to control the relative depth of the various minima (see Fig. 3). A first-order phase transition can be made to occur involving any two of these minima (with the third one metastable).

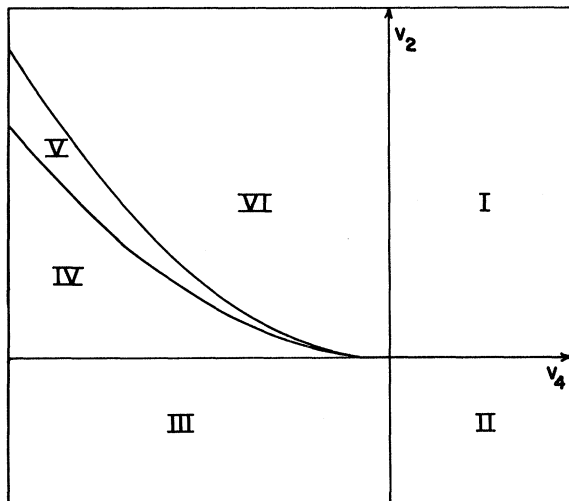


FIG. 1.  $v_2$ - $v_4$  plane. The boundary between regions VI and V is the curve  $x = -(3y)^{1/2}$ . The boundary between the regions IV and V is the curve  $x = -2y^{1/2}$ . Other boundaries are the coordinate axes.

There are a number of reasons to explore the morphology discussed so far. First, since the morphology constitutes the qualitative prediction of the theory, if it were absent the theory would simply be wrong. Second, some of the configurations of stable and metastable states may be of interest in themselves. For example, starting from a triple point [Figs. 2(g) and 3], the addition of a linear term creates a series of steps so that as one moves in the direction of the (one-dimensional) order parameter  $\mu$ , one goes through states of successively lower free energy. One may ask if the decay of the system follows these steps or if a system starting from the highest state goes directly to the lowest. This is a question about the form of the fluctuation (or "critical droplet") that effects the transition out of the metastable phase. A plausible hypothesis is that in some regions of thermodynamic phase space the decay is a one-step process; in some regions two steps are required. It might be necessary though to move slightly into region IV [Fig. 2(f) (plus linear term)] before the one step process would be observable. One can then expect that with the help of the formula<sup>15</sup>

$$R = Ie^{-\Delta F/kT} \quad (3.2)$$

(where  $\Delta F$  is the "activation energy" or energy of critical droplet and  $R$  is a rate of transition) some information could be gained about the nature of various kinds of critical droplets. Of course many assumptions would go into the use of (3.2) but it may be hoped that the conclusions would be insensitive to at least some of the assumptions that ordinarily go into estimating the rate, because we are only comparing various processes in the same physical system.

Our final point is of some fundamental interest. The coefficient of the  $\mu^3$  term,  $v_3$ , does not seem to have made any appearance in the literature of physics. The reason is that, given the physical variables known to be present, one usually has definite ideas about the dependence of the free energy on these variables—and  $\mu^3$  does not appear.

In catastrophe theory one takes the opposite view—the full development of a catastrophe takes place in a number of dimensions determined by the topology of the potential (for type-three phase transitions this dimension is four). If fewer independent physical variables are present one may get symmetry breaking or simply an absence of certain morphology. For example, if one studied ferromagnets by varying temperature but did not know of magnetic fields, then passing through the critical temperature from above, an apparent breaking of symmetry would occur. It is also possible that though one may have been unaware of external fields before the experiment, such external fields could be discovered by extreme sensitivity

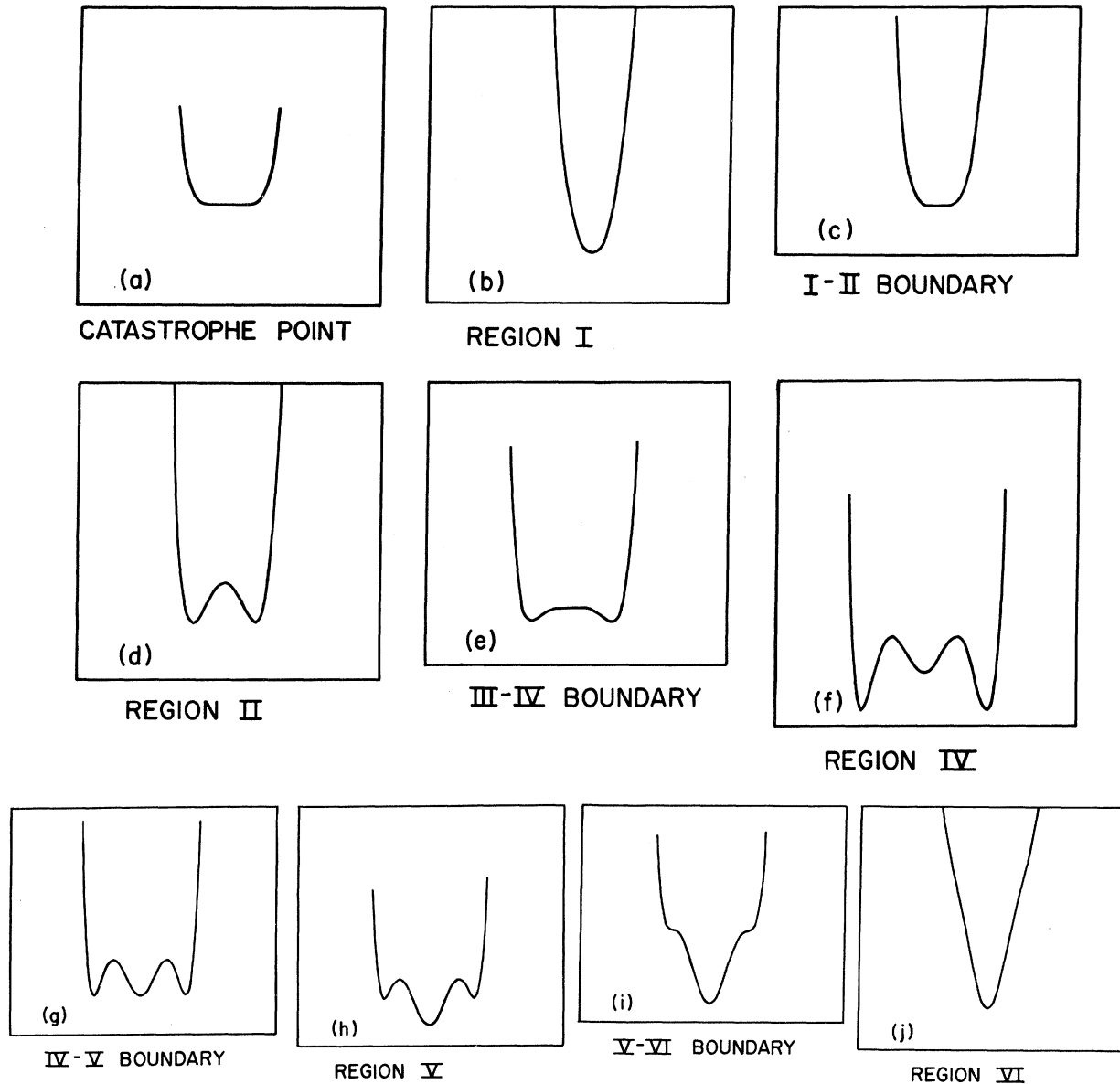


FIG. 2. (a)–(j) give the form of the free energy in the various regions of the phase space (the  $v_2$ - $v_4$  plane). [Vertical distances ( $y$ ) have been doubled relative to horizontal ones.] The curve plotted is  $y=Q(x)=x^6+ax^4+cx^2$ . (a) Catastrophe point  $a=c=0$ ; (b) region I,  $a=2$ ,  $c=2$ ; (c) I-II boundary,  $a=2$ ,  $c=0$ . This is a second-order, type-two phase transition; (d) region II,  $a=2$ ,  $c=-2$ . Curves in region III and on the II-III boundary have the same appearance; (e) III-IV boundary,  $a=-1$ ,  $c=0$ ; (f) Region IV,  $a=-3$ ,  $c=2$ ; (g) IV-V boundary,  $a=-3$ ,  $c=2.25$ . Triple point; (h) region V,  $a=-3$ ,  $c=2.5$ ; (i) V-VI, boundary,  $a=-3$ ,  $c=3$ ; (j) region VI,  $a=-3$ ,  $c=4$ .

of the system to a particular kind of perturbation, which could then be defined as the external field.

Similarly we seek meaning for  $v_3$ . We concentrate on ferroelectrics, where the classical theory has been used extensively<sup>7</sup> and we take  $\mu$  to be the polarization  $P$ . For each ferroelectric,  $v_4$  has some particular value and it is only when substances are mixed that  $v_4$  becomes a continuous variable that can pass through zero.<sup>16</sup> The coefficient  $v_1$  is

the electric field  $E$  in some direction. By symmetry, in the absence of an electric field  $v_1$  and  $v_3$  vanish, even if pressure is applied to the substance. Nonlinear effects due to  $E$  have apparently not yet indicated an  $E$ -dependent  $v_3$ ; nevertheless once  $E$  is turned on such a term might appear. Just as an amateur's guess we propose that variation of the pressure could control the relative size of  $v_3$  for given  $v_1$ .

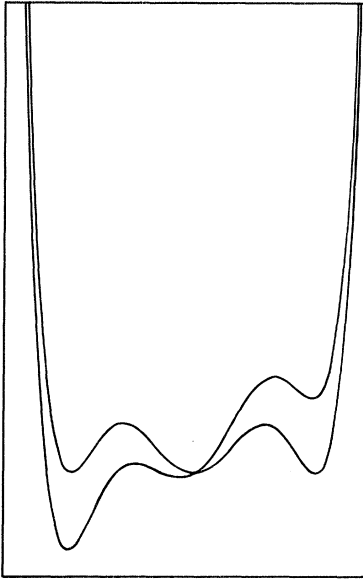


FIG. 3. Curves  $y = x^6 - x^4 + \frac{1}{4}x^2 + bx$ ,  $b = 0, 0.04$ . The  $b = 0$  curve is symmetric about  $x = 0$  and represents a triple point [Fig. 2(g)]. The vertical scale ( $y$ ) is exaggerated by a factor of 8.

The foregoing is only an attempt to suggest a way to control  $v_3$ . It may be hoped that those familiar with the various substances will find ways of producing and controlling nonzero  $v_3$  in ferroelectrics or metamagnets or perhaps in  $\text{He}^3$ - $\text{He}^4$  mixtures.

The analog of the apparent symmetry-breaking "discovery" of external fields as applied to  $v_3$  would begin with a potential in region V of Fig. 1 [see also Fig. 2(h)] and add a linear term so as to make the two left (or right) minima equal [for example, take  $V(\mu) = \mu^2(\mu^2 - \alpha^2)^2 + \epsilon\mu^2 + \epsilon\alpha\mu$ ,  $\alpha^4 \gg \epsilon > 0$ ]. Then any small term of the form  $v_3\mu^3$  would shift the system to either  $\mu \sim 0$  or  $\mu \sim -\alpha$ . A problem that might arise in making such a "discovery" is the difficulty in being sure that the new field is not in fact contributing to  $v_1$ .

Control of  $v_3$  will allow full exploration of the catastrophe, permitting a number of new phenomena to be observed. We consider a rather exotic phase transition: a line of double points turning into a line of triple points. That is, for some value of the external variables two phases coexist. As some parameter changes one of these phases goes through a second-order transition (of type two) and itself becomes two phases while the other remains relatively unchanged, leading altogether to three phases. The potential associated with this phenomenon is  $V(\mu) = Q(\mu) - Q(0)$ , where

$$Q(\mu) = \begin{cases} (\mu + 2a)^2 [(\mu - a)^2 + b]^2, & b \leq 0 \\ (\mu + 2a)^2 (\mu - a)^2 [(\mu - a)^2 + b], & b > 0. \end{cases} \quad (3.3)$$

(These polynomials are uniquely defined.) For fixed  $a$ ,  $b$  is varied. For  $b > 0$  there are equal minima of  $Q$  (or  $V$ ) at  $\mu = -2a$  and  $\mu = a$  leading to a first-order transition. For  $b = 0$  the minimum at  $\mu = a$  becomes flat [ $\sim (\mu - a)^4$ ] and if the minimum at  $\mu = -2a$  were ignored it would look like a type-two catastrophe. For  $b < 0$  there are (equal) minima at  $\mu = -2a, a \pm (-b)^{1/2}$  (Fig. 4). One may also allow  $a$  to approach zero and study this phenomenon as it approaches the type-three catastrophe (Fig. 5).

A surface of second-order (type two) transitions with vertex at the tricritical point would be another phenomenon allowed by a  $\mu^3$  term. This surface contains the lines which Griffiths<sup>1</sup> uses to characterize the tricritical point but only with a  $\mu^3$  term can these lines spread into a surface. An appropriate polynomial is  $P(\mu) = (\mu - \lambda)^4 [(\mu - \lambda)^2 + 6\lambda(\mu - \lambda)]$

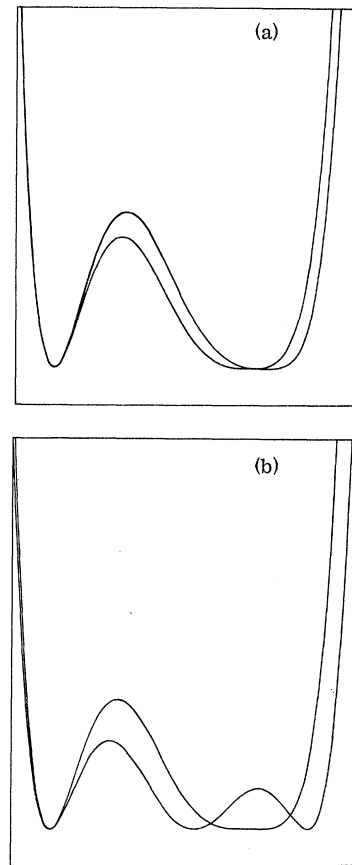


FIG. 4. Double point changes to triple point. The curve  $y = Q(x)$  is plotted.  $Q$  is given by Eq. (3.3). The vertical scale ( $y$ ) is exaggerated by a factor of 24. (a)  $a = 0.35, b = 0, 0.03$ . (b)  $a = 0.35, b = 0, -0.03$ . For  $b = 0$  there is a second-order transition (type two) in the state near  $a = +0.35$ . Varying  $b$  from positive to negative values takes the system from a triple point to a double point.

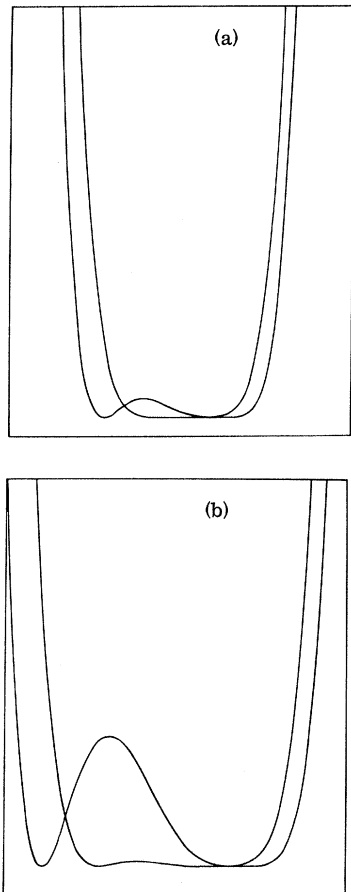


FIG. 5. Approaching the type-three critical point along a line of first-order phase transitions in which one of the states is itself at a type-two critical point. The curves plotted are  $y = (x + 2a)^2 (x - a)^4$ . (a)  $a = 0.35, 0.20$ ; vertical scale ( $y$ ) exaggerated by factor of 24. (b)  $a = 0.20, 0$ ; vertical scale exaggerated by factor 96.

$+\frac{3}{2}\beta]$ , for which there is a second-order transition so long as  $\beta \geq 6\lambda^2$ .

It may be remarked that the "meaning" for  $v_3$  which is sought after in the preceding discussion is an operational meaning within the context of our phenomenology. At best this meaning would be as well understood as that of the quantities  $v_1$  and  $v_2$ . While in Landau theory these quantities have experimental significance (e.g., electric field), in theories more closely related to microscopic models there has not been much support for direct physical interpretation of these coefficients. For example, in work on a classical system interacting via two-body forces, Lebowitz and Penrose<sup>17</sup> were able to derive a free energy involving a term  $\alpha\rho^2$ , where  $\rho$ , as density, plays a role analogous to  $\mu$  in Eq. (3.1). The coefficient  $\alpha$ , however, turned out to be related to the properties of an infinitely weak infinitely long-range potential, thus depriving it of any clear physical significance.

#### IV. SUMMARY AND CONCLUSIONS

(a) We have argued that tricritical points of all kinds (metamagnets, ferroelectrics, He<sup>3</sup>-He<sup>4</sup> mixtures) can be described by sixth-order polynomials of the form of Eq. (3.1)—that is, they are type-three catastrophes. The relation between the variable  $\mu$  appearing in (3.1) and the physical order parameter is monotonic and the assumption of a power relationship leads to predictions for critical exponents. A linear relation leads to what one generally describes as the incorrect predictions of the Landau theory.

(b) Assumptions on the form of the functions  $v_i(x)$  lead to further quantitative predictions.

(c) Calculation of specific heats requires yet more assumptions on the modes near the Jacobi mode.

(d) Minima of the constrained free energy which are not absolute minima are identified as metastable states, as in the usual mean-field theories. Fisher<sup>18</sup> has emphasized the problematic nature of any statements about thermodynamic properties of "metastable" states in view of rigorous convexity and stability results which hold for thermodynamic systems. Because of the phenomenological character of our theory and because of the apparent experimental significance of metastable states, we do not consider their appearance in our theory a disadvantage.

(e) No attempt was made to establish the nature of  $\mu$  or the functional dependence of the coefficients in the metamagnet or He<sup>3</sup>-He<sup>4</sup> cases. Their identification as type-three phase transitions was made on topological grounds.

(f) Near the catastrophe, the free energy of the Jacobi field for various stable and metastable phases can be controlled. This may be useful in studying the fluctuations that take the system out of the metastable state.

(g) There is, in principle, an additional external variable available to the experimenter (for type-three phase transitions) which has never been exploited. We have discussed morphology which will be observable once the coefficient  $v_3$  becomes amenable to experimental control. We mention, however, that the cubic term discussed by Landau<sup>14</sup> is different from that discussed by us and in our formalism is eliminated by a change of variable [see Eq. (14) of Ref. 3].

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<sup>5</sup>For a ferromagnet in a box of length  $L$  (as described, say, in Ref. 9) the Jacobi mode has wavelength  $2L$ . The mode with wavelength  $L$  has, at the critical temperature, a minimum very nearly as flat as the Jacobi mode itself. Similarly, for a system of spins on a one-dimensional lattice with nearest-neighbor interactions, although the lowest energy may be attained by orienting all spins in one direction, the energy cost for a single change of direction along the line is so slight that the energy barrier between the different orderings of the lattice is minimal.

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<sup>10</sup>The mapping  $h$  in Eq. (1.3) is a homeomorphism.

<sup>11</sup>For any given system, having found the variable  $\mu$  related to  $P$  by Eq. (2.5), the study of structural stability in terms of  $\mu$  and  $V(\mu)$  involves only smooth (at least twice differentiable) transformations of  $\mu$ .

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## Critical Behavior of a Classical Heisenberg Ferromagnet with Many Degrees of Freedom\*

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The critical behavior of a classical Heisenberg ferromagnet is studied in the limit where the spin dimensionality  $N$  is large. Corrections of order  $1/N$  to the spherical model are obtained as functions of a continuous dimension  $d$ ,  $2 < d < 4$ . Particular attention is given to the behavior near the coexistence curve. The divergence of the magnetic susceptibility below  $T_c$  as the external field vanishes is discussed through a nonlinear realization of the  $O(N)$  symmetry, as well as in the  $1/N$  and  $4-d$  expansions.

### I. INTRODUCTION

Universality of scaling behavior in critical phenomena applies only to systems with a given number  $N$  of internal degrees of freedom. This is manifest in recent works which use the  $\epsilon$  expansion technique developed by Wilson and Fisher.<sup>1</sup> This method provides systematic corrections to mean-field theory by a perturbation expansion in  $\epsilon = 4 - d$ , where  $d$  is the dimension of space. Both critical exponents<sup>1</sup> and the scaling equation of state<sup>2</sup> exhibit explicitly a dependence on  $N$ .

In this paper  $\epsilon$  is not assumed to be small, but may take any value between zero and two. The approximation now lies in the assumption that all quantities may be expanded in power of  $N^{-1}$  for  $N$  large. The motivation lies in the result of Stanley<sup>3</sup> that the limit  $N \rightarrow \infty$  of a classical Heisenberg ferromagnet, in which each "spin" has  $N$  components, is identical to the exactly soluble spherical model of Berlin and Kac.<sup>4</sup> More recently a simple diagrammatic approach has been presented in a field-theoretical framework by Wilson.<sup>5</sup> This method

gives both Stanley's result and systematic corrections in powers of  $N^{-1}$ . It is here applied to the calculation of critical exponents and of the equation of state of a magnetic system, to order  $1/N$ .

The numerical agreement of this expansion with the behavior of an ordinary magnetic system where  $N=3$  is not expected to be particularly satisfactory. In fact, the  $\epsilon$  expansion results seem to indicate that the asymptotic region in  $N$  requires at least  $N \geq 8$ .

Therefore, the aim of this  $1/N$  expansion is rather to give theoretical information which the  $\epsilon$  expansion is not able to provide. In particular, our interest was to study the behavior of the system near the coexistence curve, i.e., below the critical temperature when the applied magnetic field  $H$  tends to zero. In this region there are two different characteristic lengths associated with transverse and longitudinal magnetic susceptibilities. It is not clear that the  $\epsilon$  expansion in which the coupling constant is fixed to induce the expected scaling only in the longitudinal correlation length, does not break down in the vicinity of the coexis-