Phase diagrams and higher-order critical points*

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A classification scheme is presented for the different entities one might expect to find in phase diagrams of fluid mixtures (or other systems where the phases do not break the symmetry of the Hamiltonian) when critical phenomena are present. These include critical points and critical end points of various sorts, higher-order critical points, and entities coexisting in distinct phases. The classification scheme employs the topological properties of the phase diagram, in a space of field variables (temperature, chemical potentials), in the immediate vicinity of the point in question. A graphical method is given for representing some of the topological information in the phase diagram. The entities obtained using a Landau model with one order parameter are discussed and some preliminary results are presented for the case of two order parameters. A phase diagram for a possible fluid analog of the two-dimensional three-state Potts model is described.

I. INTRODUCTION

This paper deals with two problems. The first is the classification and description of higher-order critical points of the sort one might expect to find in ordinary fluid mixtures,[1] in terms of their phase diagrams. The second is to find a set of rules for drawing phase diagrams for complex thermodynamic systems when critical phenomena are present. These two problems are intimately connected, and from the point of view adopted in this paper they are almost equivalent: an acceptable phase diagram can contain only a limited class of elements including points of ordinary m-phase coexistence together with ordinary and higher-order critical points. The Gibbs phase rule places specific constraints on acceptable phase diagrams (e.g., no more than three phases can coexist at a single point on the pressure-temperature plane for a pure substance). One might expect analogous constraints for phase diagrams involving critical points, and we will present some suggestions as to what they are.

Higher-order critical points are not limited to ordinary fluid mixtures but also occur in superfluids and magnetic solids.[2] The latter are outside the scope of this paper because the phases involved break certain symmetries of the Hamiltonian, and these symmetries must be taken into account in constructing phase diagrams. For the same reason, the Gibbs phase rule requires some modifications when applied to these "symmetry-breaking" systems.

The phase diagrams of interest in modern statistical mechanics are not restricted to the traditional set of variables available in experiments: temperature, composition, and the like. It is often valuable to augment the variable space by adding certain parameters which appear in the Hamiltonian of the system (e.g., strength of some particular interparticle potential) or in a suitably augmented Hamiltonian (e.g., a staggered magnetic field for an antiferromagnet). We expect the phenomenology developed in this paper to apply to these generalized phase diagrams in the same way as to phase diagrams using traditional variables, provided, of course, that symmetry breaking plays no essential role. Thus the term "fluid mixtures" as it appears below is an abbreviation for the sort of situation exemplified by, but not restricted to, such mixtures.

We will only discuss phase diagrams in a thermodynamic space spanned by "field" variables[3]: those which are always the same in two coexisting phases, such as temperature and chemical potentials. Such diagrams are invariably simpler than the ones constructed using "densities," such as mole fractions, mass density, and entropy. Further, the diagrams in a field space contain all the information about the topological properties of the other diagrams. Since these are the properties of interest in this paper, there is no loss in generality if only field-space diagrams are considered. In connection with the previous paragraph, it may be noted that when the Hamiltonian of a system depends on a set of real (scalar) parameters, these will typically appear as field variables in statistical mechanics.

Previous work dealing with the geometrical form of phase diagrams near higher-order critical points is found in Refs. 4–6. The proposal of Chang, Hankey, and Stanley,[4] though somewhat vague and failing to distinguish adequately (in our opinion) between situations with and without symmetry breaking, is similar in spirit to the one presented below. Zernike[5] has discussed the number of components necessary in a fluid mixture in order to observe a critical point of the sort discussed in Sec. IV B below. Schulman[6] and his collaborators have used the theory of catastrophes for classifying critical points. While we are indebted to Ref. 6 for various ideas, our own approach is different in some important respects. Catastrophe theory (so far as we understand it) provides a phenomenological model of phase transitions with results at critical points which are very similar, if not identical, to those predicted by the Landau model (Sec. IV below). (We are not convinced by the claims[6,7] that catastrophe theory is superior to the Landau model in allowing for nonclassical exponents.) By contrast, our system of classifying higher-order critical points in terms of their phase diagrams is not wedded to any particular scheme for generating them, although as a practical matter we must employ phenomenological models to produce specific examples.

An outline of the remainder of this paper is as follows. Section II contains a general discussion of phase diagrams from the point of view adopted in this paper. The notions of codimension, characteristic ball, and topological equivalence, as applied to phase diagrams, are introduced together with a graphical representation of certain features of phase diagrams. The characteristic balls and graphs for multiple-phase coexistence, critical points, and critical end points are the subject of Sec. III. Section IV contains a discussion of higher-order critical points as found in Landau models with one order parameter (treated in detail) and two order parameters (a preliminary treatment), and certain geometrical notions which aid one in guessing the forms of possible characteristic balls not given by the Landau models. A brief summary, together with a list of unanswered questions, is found in Sec. V.

II. GENERAL PROPERTIES OF PHASE DIAGRAMS

A. Examples and a definition

The phase diagram for a pure substance in the pressure p, temperature T plane has, typically, features like those indicated schematically in Fig. 1. The two-dimensional regions α, β, γ occupied by the different phases are separated by curves along which two phases coexist. These two-phase curves terminate at triple or three-phase points (a, b), or critical points (c), or on the boundaries of the diagram.

For a binary mixture there are three independent fields, e.g., p, T, and the chemical potential or activity of one of the components. The three-dimensional regions occupied by different phases are separated by two-phase surfaces which terminate on three-phase lines or lines of critical points. In addition, the regions of two- and three-phase coexistence and critical points can terminate on the boundaries of the diagram.

In general one has a thermodynamic space Y which is some region in an s-dimensional real vector space spanned by the (field) variables y_1, $y_2, \ldots, y_s$. Inside Y there will be points of two-phase, three-phase, etc., coexistence along with critical and higher-order critical points, critical end points, and the like. We denote by Q the totality of such points, which we expect will form a closed set (in the usual topology) relative to Y. The *phase diagram* shall be the pair (Y, Q), and we will occasionally refer to Y or Q as the phase diagram when the other member of the pair is clear from context. A subset Y' of Y is a phase diagram (Y', $Y' \cap Q$).

B. Acceptable phase diagrams

Theory and experiment together suggest that Q can have only certain restricted forms and cannot be an arbitrary subset of Y. The rules which specify an "acceptable" phase diagram Q are, at present, phenomenological principles whose range of applicability is not known. It is a challenging theoretical problem to relate them to the fundamental principles of statistical mechanics. With out any attempt at completeness, we may mention the following as reasonable phenomenological rules.

Each point in Y belongs to one of a limited number of acceptable types of points, each type (or "entity") being determined by the properties of the phase diagram in the immediate vicinity of the point. For example, a point in Y which is not in Q corresponds to a single phase (we shall call it a one-phase point); such a point is characterized by the fact that it has an open neighborhood which

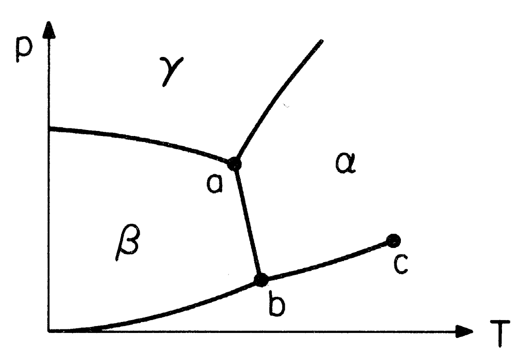

FIG. 1. Schematic phase diagram for a pure substance.

does not intersect Q.

Points of a given type lie on smooth manifolds (curved hypersurfaces) in Y whose codimension κ is characteristic of the entity in question. By *codimension* we mean the dimension of the space Y minus the dimension of the manifold. For brevity we shall say that an entity "has" a given codimension when we mean that a manifold of points corresponding to this entity is of that codimension. For example, two-phase points lie on manifolds of dimension one less than Y, so $\kappa = 1$, while critical points have $\kappa = 2$. We prefer to leave undefined the precise degree of smoothness of a smooth manifold, since it is unimportant for present purposes. A reasonable assumption is twice continuously differentiable, though the second derivatives may diverge upon approaching a boundary of the manifold.

C. Characteristic balls

If the space Y is two-dimensional, a triple or three-phase point can be easily identified by the three two-phase lines which come together at this point. At a triple line in a three-dimensional space, three two-phase surfaces come together, but if we take a two-dimensional section of the space which intersects, and is not parallel to, the triple line at some point, this section again contains three two-phase lines meeting at the triple point. Thus this two-dimensional section is characteristic of triple points and can be used to identify such a point no matter what the dimension of the space Y.

The following definitions are an attempt to make the foregoing more precise. Two phase diagrams (Y_1, Q_1) and (Y_2, Q_2) are *topologically equivalent* if there is a homeomorphism (one-to-one mapping which, together with its inverse, is continuous) from Y_1 onto Y_2 which maps Q_1 onto Q_2. The ball $B_r(z)$ of radius r centered at z, the set of points y in Y for which $|y-z|$ is less than r, will be called a *typical* ball for the point z if it is topologically equivalent as a phase diagram to any ball of smaller radius centered at z. A *characteristic* ball is a typical ball whose center is unique in the sense that any homeomorphism which carries $B_r(z)$ and $B_r(z) \cap Q$ onto themselves must map z onto itself. Figure 2 shows examples of typical, nontypical, and characteristic balls in a two-dimensional phase diagram.

The typical ball labeled 3 in Fig. 2 is an example of a *cylinder* of a characteristic ball, or *characteristic cylinder*. We define this object more precisely as follows. Let (B, Q) be a characteristic ball in a space V, and C a unit ball in a space W. In the product[8] $V \times W$ of ordered pairs (v, w) we

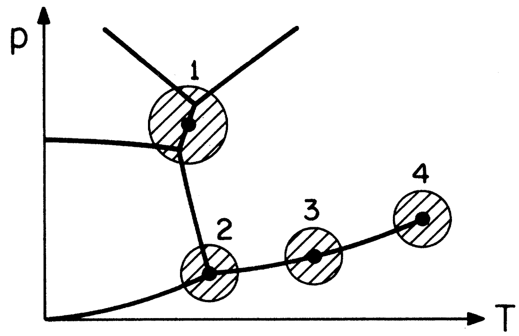

FIG. 2. Phase diagram with the balls (in this case disks) surrounding certain points indicated by light cross hatching. Ball 1 is nontypical while 2, 3, and 4 are typical; 2 and 4 are characteristic while 3 is a cylinder.

define

$$B' = \{(v,w) : v \in B, w \in C\},$$

$$Q' = \{(v,w) : v \in Q, w \in C\}.$$

Then (B', Q') and any phase diagram topologically equivalent to it is by definition a cylinder of the characteristic ball B.

We can now make the phenomenological rules in Sec. B above more precise. We assume that for any $y \in Y$ in a phase diagram (Y, Q) there is a positive r such that $B_r(y)$ is a typical ball which is either a characteristic ball or the cylinder of a characteristic ball. Two points in Y are of the same type, or correspond to the same entity, if the corresponding characteristic balls are topologically equivalent. We assume that the totality of points corresponding to a particular entity (such as three-phase coexistence) lie on one or more smooth manifolds with codimension equal to the dimension of the characteristic ball. In addition, only typical balls topologically equivalent to one of a certain catalog of *acceptable* characteristic balls, or their cylinders, are permitted in an acceptable phase diagram. Sections III and IV of this paper are devoted to devising such a catalog.

Homeomorphisms are probably not the ideal transformations to use in defining equivalence classes of points in a phase diagram. They do not preserve smoothness of the manifold or the geometrical properties embodied in the 180° rule[9] and its analogs for $m(\geq 3)$-phase coexistence. Nonetheless, topological equivalence provides a simple classification scheme which can then be further refined.

D. Phase-diagram graphs

Since phase diagrams in a space of dimension greater than 3 are difficult to visualize, it is useful to construct a graph which contains some of the topological information in the diagram. Each separate manifold in the phase diagram is represented by a vertex, and vertices corresponding to manifolds of the same codimension are placed in the same column (or row if one prefers). If one manifold lies on the boundary of another with one less codimension, a directed edge is drawn from the vertex corresponding to the first manifold to that corresponding to the second. (The arrow on an edge, in the direction of decreasing codimension, may be omitted when this direction is obvious, as in Fig. 5.) Figure 3 is the graph for the phase diagram in Fig. 1.

The phase graph shows what happens on the boundaries of different manifolds. Of course a manifold may terminate on the boundary of a phase diagram. For this reason such points on the boundary of the diagram may be considered a separate "boundary entity" of codimension one more than that of the original manifold, and a corresponding vertex added to the graph (this has not been done in Fig. 3).

A *characteristic graph,* or phase-diagram graph for a characteristic ball, has a unique vertex at the maximum codimension, and all other vertices can be reached from it following a chain of edges in the direction of decreasing codimension. Two such graphs are equivalent if there is a one-to-one mapping of the vertices of one onto vertices of the same codimension in the other which simultaneously carries the edges of the first onto those of the second. This equivalence can be used in place of the topological equivalence of characteristic balls discussed previously in order to classify the different points in a phase diagram. Obviously, equivalence of the characteristic balls implies equivalence of the corresponding graphs, but not the reverse. We have not yet discovered any cases in which two inequivalent *acceptable* characteristic balls correspond to equivalent graphs.

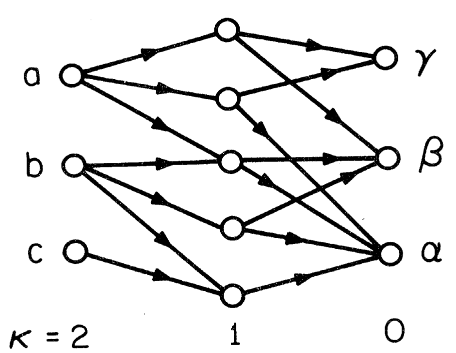

FIG. 3. Phase-diagram graph for the diagram in Fig. 1. Codimensions are noted at the bottom of each column.

III. COEXISTENCE OF PHASES AND CRITICAL POINTS

A. Special sections and symmetries

Under certain circumstances, one encounters apparent violations of the principles set forth in Sec. II and extended below. An example is the case of "special sections," illustrated in a two-dimensional phase diagram (e.g., the p, T plane for a pure substance) in Fig. 4. Situation (b) in this figure, in contrast to (a) and (c), is not permitted by the Gibbs phase rule because all four phases α, β, γ, and δ coexist at the center of the diagram. Imagine, however, that one could vary a parameter in the Hamiltonian so that the phase diagram changed continuously from (a) to (c). Clearly (b) would occur for some value of the parameter, and in this sense it is not an unreasonable diagram. Indeed, if one adds the parameter just mentioned to the other two field variables used in Fig. 4, the resulting thermodynamic space is three-dimensional and the center of Fig. 4(b) is perfectly acceptable as a point of four-phase coexistence in this augmented variable space. The apparent anomaly in Fig. 4(b) arises from taking a special section of the three-dimensional space which just happens to pass through the four-phase point. In this paper we shall always suppose that situations such as Fig. 4(b) can be taken care of by suitably augmenting the variable space, and we shall not discuss the rules which govern the phase diagram in a special section.

A similar problem is posed by systems whose Hamiltonians possess special symmetries. In this situation a diagram as in Fig. 4(b) could be the result of a symmetry requirement which caused the parameter to have precisely the right value. This subject is an interesting one but beyond the scope of the present paper, in which we will assume that no such symmetries occur.

B. Coexistence of m phases

The Gibbs phase rule states that the coexistence of m phases in a system composed of c components has

$$f = c + 2 - m \tag{3.1}$$

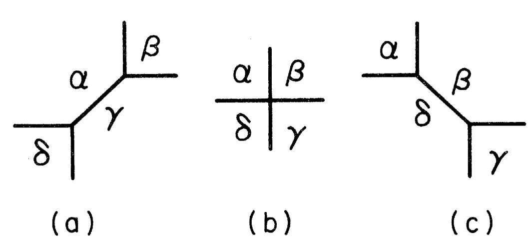

FIG. 4. Diagram showing four phases in a plane.

degrees of freedom. In a field-space phase diagram, f is the dimension of the manifold of m-phase coexistence. Since there are $c+1$ independent fields, the manifold has a codimension κ equal to $c+1-f$, or

$$\kappa = m - 1. \tag{3.2}$$

While (3.1) and (3.2) are equivalent, the latter is to be preferred when discussing field-space phase diagrams because there is no dependence on the number of components, and the relationship remains valid in the presence of chemical reactions or when one augments the thermodynamic space using parameters in the Hamiltonian.

With the same degree of rigor used to derive (3.1), one can show (Appendix A) that the characteristic ball for m-phase coexistence is unique (up to topological equivalence) and contains precisely one manifold of points where a given (nonempty) subset of the m phases, and no others, coexist. The characteristic graph has one vertex for each nonempty subset of the m phases, and a directed edge is drawn from one vertex to another if the former subset is obtained by adding one phase to the latter. The case $m=3$ is shown in Fig. 5.

C. Critical points and critical end points. Elementary and composite entities

An ordinary critical point with codimension $\kappa = 2$ occurs when two coexisting phases become identical. The characteristic ball is number 4 in Fig. 2. A critical end point [Fig. 6(a)] with $\kappa=3$ occurs when two coexisting phases become identical in the presence of a third. Figure 7 shows the phase diagram near such a point. Two phases may also become identical in the presence of two [Fig. 6(b)] or more additional phases. Each additional phase increases the codimension by one.

The different kinds of critical end points represent distinct possibilities in terms of phase diagrams, but the presence of the additional phases is not expected to have much influence on the critical phenomena. Two phases coexist when their free energies[10] are equal, but the properties of one of the phases are not expected to change significantly if the fields are altered slightly so that the other phase is absent. With enough thermodynamic degrees of freedom, one can achieve critical phenomena simultaneously in two distinct phases [Fig. 6(c)], but the mutual influence of the critical phenomena is probably restricted to their effects on the free energies of the respective phases.

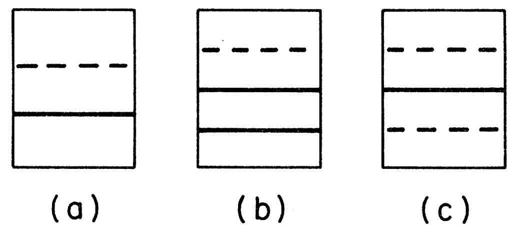

FIG. 6. A schematic diagram of a container with several fluid phases. Solid lines indicate meniscuses and broken lines meniscuses which have just disappeared at a critical point.

It is convenient to use a product notation for situations such as the ones just discussed. If S and U stand for two entities, SU or US will denote the entity which corresponds to having S and U present simultaneously in two coexisting phases with distinct properties. Let A stand for a simple single phase and B an ordinary critical point. Three-phase coexistence is AAA or A^3 in this notation. The critical end points in Figs. 6(a) and (b) are BA and BA^2, respectively, while Fig. 6(c) is B^2.

We introduce two hypotheses concerning such products: (i) The codimension κ of SU is given in terms of those of S and U by

$$\kappa(SU) = \kappa(S) + \kappa(U) + 1. \tag{3.3}$$

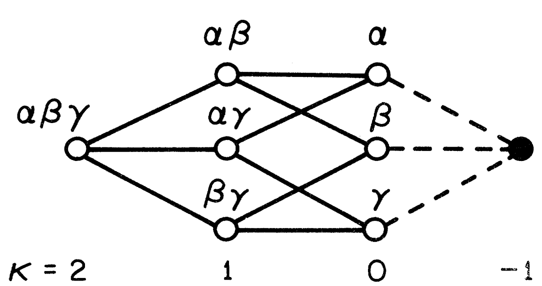

FIG. 5. Characteristic graph for three-phase coexistence. Phases are labeled α, β, and γ. Dotted lines and the vertex at $\kappa=-1$, normally absent, are added to form the augmented graph (see Appendix B).

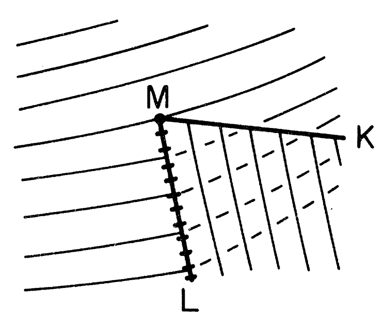

FIG. 7. Phase diagram in a three-dimensional field space near a critical end point M at the intersection of a line of critical points KM and a triple line LM.

(ii) The characteristic ball for SU is uniquely determined (up to topological equivalence) by the characteristic balls of S and U.

The first hypothesis seems reasonable in the light of the usual arguments used to justify the phase rule. The second is given support by the technique described in Appendix B for generating the characteristic ball of SU from those of S and U. We are not entirely sure, however, that this technique is correct.

The second hypothesis greatly simplifies the task of constructing a catalog of acceptable characteristic balls. We define a *composite* entity as one which is the product of two (or more) entities in the sense just discussed. An *elementary* entity is one which is not composite. We shall assume that a composite entity is acceptable if and only if it is a product of acceptable elementary entities. Our task then becomes one of finding all the acceptable elementary entities. They should all, with the exception of A, be some sort of critical point.

As noted previously, the points where the manifold of some entity intersect the boundary of Y may be thought of as a special boundary entity. A possible notation is Sa for the boundary entity[11] if S is the entity in the interior of Y. The former has a codimension one greater than the latter.

IV. HIGHER-ORDER CRITICAL POINTS

A. General remarks

If the ideas in Sec. III are correct, the local properties of an acceptable phase diagram are completely specified by a catalog giving all acceptable elementary characteristic balls. We know of no method of obtaining these by purely thermodynamic considerations. Alternative possibilities are experiments on real materials, calculations using statistical mechanics, and guesses based on geometrical intuition. The last is unlikely to prove a reliable guide, though we discuss one application of it in Sec. IV D. Experiments on fluid mixtures are potentially a very valuable source of information, but to date have revealed nothing more complex than tricritical points.

Thus we must turn to statistical mechanics for the bulk of our information on higher-order critical points. Exact model calculations of phase coexistence are rather rare. Typical approximation methods, if they yield a consistent thermodynamics, give results qualitatively similar to mean-field theory. Even though their detailed predictions for critical phenomena are in error, such approximations often yield phase diagrams with correct topological features. Landau[12] has shown how the essential qualitative results of these approximations can be obtained by simply expanding a thermodynamic potential as a power series in an order parameter. Since we are only concerned with qualitative features of phase diagrams, we shall follow Landau's procedure and make no direct reference to underlying statistical models.

Series expansion methods and renormalization group calculations give better descriptions of critical phenomena than Landau's procedure. Neither method is very effective in locating m-phase coexistence surfaces, and thus they have not, to date, added much to our knowledge of the qualitative features of phase diagrams. In addition there are a number of exactly soluble models in one and two dimensions. The resulting phase diagrams are either in qualitative agreement with Landau's approach and the type of diagrams observed in experiments (on three-dimensional system), or so completely different[13] as to deserve a separate discussion beyond the scope of this paper. Of course, it may very well be the case that the class of acceptable characteristic balls depends on the class of systems one is willing to consider, and in particular on the dimensionality.

In what follows we shall discuss the Landau model with one order parameter in some detail. The case of two order parameters is much more difficult and we present only preliminary results. Additional novelties are to be expected from models with three, four, etc., order parameters, but only at higher codimensions, and we do not discuss them. A characteristic ball which could be the "fluid equivalent" of the two-dimensional three-component Potts model is presented in Sec. IV D.

B. Landau model with one order parameter

Let the thermodynamic potential Ψ be a real polynomial in the order parameter x:

$$\Psi = a_0 + a_1 x + a_2 x^2 + \cdots + x^{2q}. \tag{4.1}$$

As the notation indicates, we assume the polynomial is even and the coefficient of the highest power is 1. (It suffices to assume that it is positive.) The a's are thermodynamic field variables spanning a space Y. For a given choice of a's, the stable thermodynamic state is identified with the x which minimizes Ψ. If the minimum occurs for m distinct values of x, these are identified with m coexisting phases. Local, as opposed to absolute or global, minima of Ψ are to be ignored.

Clearly a_0 has no influence on the thermodynamic state. Thus, we may without loss of generality choose it (as a function of the remaining a's) so that the minimum value of Ψ is always zero. Such a Ψ can be written in the form[14]

$$\Psi = \prod_{j=1}^{q} [(x-b_j)^2 + d_j], \tag{4.2}$$

where the b's and d's are real, the d's are nonnegative, and at least one of the d's is zero. It is convenient to represent Ψ by a "configuration," a set of points (b_j, d_j) in the b, d plane (see Fig. 8).

If m of the d's are zero and the corresponding b's are distinct we have m-phase coexistence [see Fig. 8(a), $m = 2$]. As this requires $m-1$ additional constraints on the d's (we have already assumed that one of them is zero), the manifold of m-phase coexistence in Y has codimension $m-1$, as expected. A critical point occurs if two of the d's are zero and the corresponding b's coincide [Fig. 8(b)]. The additional constraint on the b's means the codimension κ is one more than for two-phase coexistence; hence $\kappa = 2$.

From plots such as in Fig. 8 it is evident that all points of m-phase coexistence lie on the same manifold, since the configuration in the b, d plane for one of them can be continuously transformed into the other, while at the same time always maintaining m d's equal to zero and the corresponding b's distinct. Similarly there is only one manifold of critical points. However, there are two distinct manifolds of critical-end points, since it is impossible to go continuously from (c) to (d) in Fig. 8 without having some configuration which is not a critical end point. We shall label the manifolds corresponding to Figs. 8(c) and (d) as BA and AB, respectively, even though the characteristic balls are topologically equivalent.

A tricritical point C with codimension 4 arises in the Landau model when three d's are zero and the corresponding b's coincide. It is evident, using continuity in the b, d plane, that the manifold of tricritical points is on the boundary of two manifolds of critical end points AB and BA. Its characteristic graph is shown in Fig. 9.

In general, a critical point of order r with codimension $2r-2$ comes about if r d's are zero and the corresponding b's coincide. A possible notation is D, E, etc., for $r = 4, 5$, etc. The characteristic graph for such a point is easily constructed by separating the coincident points into clusters on the b axis, with the codimension decreasing by 1 for each separate cluster produced. If a cluster consists of only one point, the corresponding d may be made positive, again decreasing the codimension by 1. By repeating in every possible way these two processes of separation (along the b axis) and "evaporation" (off the b axis), one obtains all the manifolds in the characteristic ball. Manifolds of composite entities are conveniently labeled by giving the symbols of the different elementary entities in the order in which they occur on the b axis. Two manifolds are distinct if the elementary entities occur in a different order. Figure 10 shows the characteristic graph of D.

It should be possible to construct the characteristic ball, as well as the characteristic graph, by means of continuous variation of configurations in the b, d plane. Thus far we have not found an effective method of doing so. One special feature of this model may be noted, however. Due to the fact that the order parameter is one dimensional, it is never possible to continuously interchange two phases while remaining on a manifold of two-phase coexistence. More generally, the order of m coexisting phases is always preserved under continuous variations which take place on the m-phase manifold. It seems unlikely that this feature will always be true in Landau models with two or more order parameters.

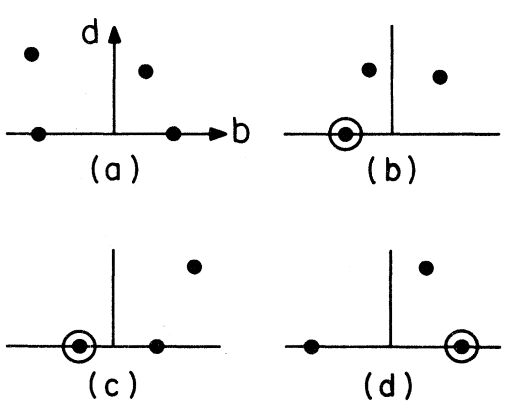

FIG. 8. Configurations in the b, d plane representing (a) A^2, (b) B, (c) BA and, (d) AB. Where two points coincide, one of them is indicated with an open circle.

C. Landau model with two order parameters

Let Ψ be a real polynomial in the variables x and y,

$$\Psi = \sum_j \sum_k a_{jk} x^j y^k, \tag{4.3}$$

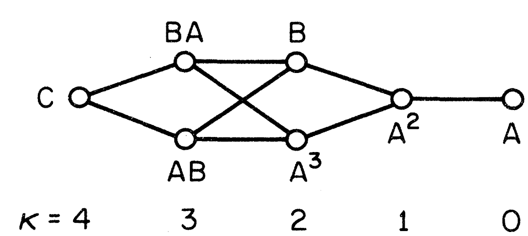

FIG. 9. Characteristic graph for a tricritical point C.

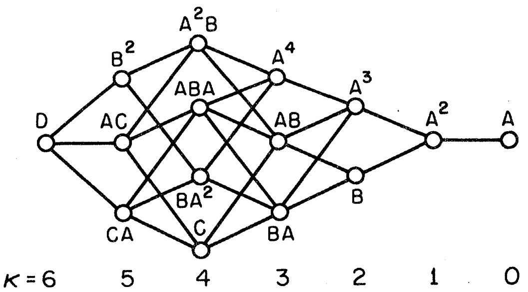

FIG. 10. Characteristic graph for a fourth-order critical point D.

with the coefficients of the highest powers chosen so that as x^2+y^2 becomes infinite, Ψ diverges to $+\infty$. The stable thermodynamic phase is the pair (x, y) for which Ψ is a minimum, and multiple minima imply multiple-phase coexistence. The coefficients a_{jk} span a thermodynamic space Y and the codimension of a manifold in this space is determined by the number of equations involving the coefficients which are needed to insure the existence of the entity (e.g., a critical point) in question. The coefficients must also satisfy certain inequalities, but these determine the boundary of the manifold(s) and not the codimension.

We may without loss of generality suppose that a particular elementary entity of interest to us occurs at the origin $x=y=0$. Such a requirement adds two constraints to the coefficients, so that in calculating the codimension of an entity we should subtract two from the number of equations.

In order that the origin be a minimum we must have

$$a_{10}=a_{01}=0 \tag{4.4}$$

and

$$4a_{20}a_{02}-a_{11}^2 \geq 0. \tag{4.5}$$

If (4.5) is a strict inequality, the origin is a local minimum, and additional inequalities on the coefficients will ensure it is a global minimum corresponding to a one-phase point. The codimension $\kappa=0$ is found by subtracting two from the number of constraints, two, in (4.4). For a critical point to occur at the origin, (4.5) must be an equality. We distinguish two cases: (i) Either a_{20} or a_{02} or both are positive. (ii) All quadratic terms vanish: $a_{20}=a_{11}=a_{02}=0$.

In case (i) there is a unique straight line through the origin along which the curvature of Ψ at the origin vanishes. Without loss of generality we may assume that this line coincides with the x axis, or

$$a_{20}=a_{11}=0, \tag{4.6}$$

while a_{02} is positive. Let the equation

$$\frac{\partial \Psi}{\partial y}=0 \tag{4.7}$$

define a function $y_0(x)$. Using the conditions just given, one can show that in a sufficiently small neighborhood of the origin, $y_0(x)$ is single valued and can be written as a power series in x starting with x^2 or a higher power. Replacing y by $y_0(x)$ in (4.3) yields a power series in x for Ψ along the curve defined by (4.7). We can now utilize the results of Sec. IV B above: to obtain an rth-order critical point all derivatives of Ψ with respect to x along $y_0(x)$, of order less than or equal to $2r-1$, vanish. Of course certain inequalities on the a_{jk} are needed to insure that Ψ does not have a minimum value away from the origin which is less than its value at the origin.

Strictly speaking, we must relax the constraints (4.4) and (4.6) to obtain a complete analogy with the one-order-parameter Landau model previously discussed. However, as long as these coefficients are sufficiently small, the curve $y_0(x)$ is single valued with a power-series expansion in the neighborhood of the origin, and Ψ along this curve is a power series in x. We must assume that a_{02} has a fixed positive value.

In case (ii) all the quadratic coefficients vanish, and therefore if the origin is to be a minimum all the cubic terms must also be zero:

$$a_{jk}=0 \quad \text{for all } j+k \leq 3. \tag{4.8}$$

There are nine equations in (4.8), which means the corresponding entity has codimension 7. We shall provisionally label it D_2. It appears to be the entity of lowest codimension which arises in the two-parameter but not in the one-parameter Landau model.

Our investigations of D_2 have not progressed very far. We have not even been able to show that it is a single entity. [As well as (4.8) there must be inequalities for higher-order coefficients, and it is conceivable that different sets of inequalities give rise to distinct characteristic balls.] The objects which Fisher and Nelson[15] have termed "bicritical" and "tetracritical" points occur as (different) special sections of D_2. It is clear that four-phase points occur in the vicinity of D_2 (hence the symbol D), and it seems unlikely that a larger number of phases coexist in its vicinity. A preliminary study indicates four manifolds of D in the characteristic ball of D_2, but we have been unable to construct the complete characteristic graph.

Of course, there will be additional higher-order critical points in the model with two order parameters, but at present we have no idea what they are. Models with more than two order parameters should lead to still more possibilities. However, the higher codimensions of these exotic points imply that they may be ignored in simple phase diagrams. For example, the point analogous to D_2 in a model with three order parameters, where the linear, quadratic, and cubic coefficients of the polynomial all vanish, should have codimension 16.

D. Geometrical principles for constructing characteristic balls

It would be interesting if one could express necessary and sufficient conditions for an acceptable characteristic ball in purely geometrical form without reference to a particular model of a phase transition. Our efforts in this direction have not had much success. If the class of acceptable characteristic balls depends on the class of Hamiltonians considered, then purely geometrical principles will obviously not suffice. Nonetheless, geometrical intuition may play a useful role when combined with other information.

All characteristic balls we have examined satisfy the following three principles, where κ is the dimension of the ball, or equivalently, the codimension of the entity at its center: (i) All entities occuring in a characteristic ball at points other than the center must themselves be acceptable. (ii) There is at least one manifold of an entity of codimension $\kappa-1$ in the characteristic ball. (iii) Every pair of manifolds of codimension $\kappa-1$ in the characteristic ball is connected by a manifold of codimension $\kappa-2$. An equivalent statement is that for any pair of vertices of codimension $\kappa-1$ in the characteristic graph there is a vertex of codimension $\kappa-2$ joined by single edges to each vertex of the pair.

We explored the implications of these rules in connection with an "erasure" procedure for producing characteristic balls for elementary entities. One starts with the characteristic ball of m-phase coexistence and then "erases" (removes from Q) certain of the two-phase manifolds, so that the phases on either side are no longer distinct but from a single phase, as illustrated in Fig. 11 for $m=3$. We examined all the possibilities for $m=3, 4$, and 5, and a large number of possibilities for $m=6$. For $m \leq 5$ the only elementary entities produced by erasure which survived the three rules were one-phase (A), critical (B), and tricritical (C) points. We were unable to generate D_2 with $m=8$, which probably means that the erasure procedure (rather than the rules) is too restrictive.

The procedure did yield one interesting possibility for $m=6$, codimension 5: a characteristic

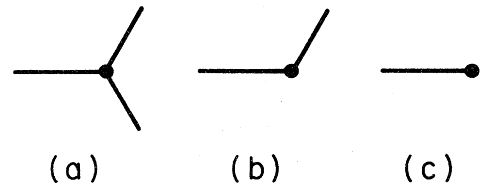

FIG. 11. Erasure procedure: (a) three-phase coexistence where three two-phase manifolds (lines) meet. The result of erasing one or two of the two-phase manifolds is shown in (b) and (c), respectively.

ball which could be the fluid analog of the three-state Potts model in two dimensions.[16,17] The ball is easiest to describe in terms of an erasure procedure which is slightly different from the one discussed above. A two-dimensional space X contains a three-phase characteristic ball, as in Fig. 11(a). Let T be a three-dimensional space of "times" $t=(t_1, t_2, t_3)$. A phase diagram in the space[8] $X \times T$ is constructed as follows. For $t_j<0$, the jth two-phase line is present in X, but it is erased when $t_j=0$ and remains absent for $t_j>0$. The ordered pairs (x, t) such that x is in one of the two-phase lines which has not yet been erased for this t constitute a set Q^* whose closure is Q. By setting $t_1=t_2=t_3$ one obtains a special section topologically equivalent to Fig. 2 in Ref. 16. This proposal for the characteristic ball is, of course, nothing more than an educated guess in the absence of more detailed calculations on, or a better theoretical insight into, the corresponding Potts model. It has one topological feature worth mentioning: It is possible, in the immediate vicinity of the critical point, to interchange two phases while they are coexisting with each other by following a suitable path on the two-phase manifold, a process not possible near critical points described by the one-parameter Landau model.

V. SUMMARY AND REMAINING PROBLEMS

Our scheme for describing acceptable phase diagrams and classifying higher-order critical points consists of the following principal items.

(i) Each point in an acceptable phase diagram in field space must be at the center of an acceptable characteristic ball or cylinder.

(ii) Two characteristic balls correspond to the same entity (e.g., two-phase coexistence) if they are topologically equivalent.

(iii) Acceptable entities are either composite or elementary. The characteristic ball of a composite entity is uniquely determined by the characteristic balls of the elementary entities of which it consists. Hence a catalog of characteristic balls for all acceptable elementary entities determines all acceptable characteristic balls. These elementary entities, apart from the one-phase point, are some sort of critical point.

(iv) Some of the topological information present in a phase diagram, and in particular in a characteristic ball, may be conveniently represented in terms of a graph.

(v) The Landau model with one order parameter yields rth-order critical points with codimension $2r-2$ for $r=2,3,4,\ldots$.

(vi) The Landau model with two order parameters yields all the critical points of the model with one-order parameter, and additional points starting with one at codimension 7.

There may very well be serious flaws in the proposals in this paper which vitiate its scheme for describing phase diagrams. Assuming that this is not the case, the following questions remain open.

(i) What are the rules for phase diagrams which are special sections?

(ii) What are the rules for phase diagrams in which symmetry breaking plays a role?

(iii) Should the equivalence of different features in a phase diagram be discussed in terms of a more restricted class of transformations than homeomorphisms?

(iv) The assertion that the characteristic ball for a compound entity is uniquely determined in terms of its constituents needs to be placed on a firmer basis (assuming it is correct).

(v) What is the complete catalog of higher-order critical points which can be produced by a Landau model with n order parameters, $n \geq 2$?

(vi) Are there necessary and/or sufficient geometrical conditions for an acceptable characteristic ball?

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The research described in this paper has benefited from a number of suggestions and criticisms by Professor J. C. Wheeler.

APPENDIX A: CHARACTERISTIC BALLS FOR m-PHASE COEXISTENCE

Let the thermodynamic space Y have dimension $m-1$ and let $f_j(y)$ be the free energy[10] of phase j as a function of $y \in Y$. We assume that the point of m-phase coexistence where all the f's are equal is the origin, $y=0$, and that their common value at this point is zero. Then to a first approximation, assuming the f's are smooth functions, each f_j can be replaced by a linear functional:

$$f_i(y) = -[\phi_j, y], \tag{A1}$$

where ϕ_j is an element of the dual space[18] Y^*.

We assume the ϕ's form an $(m-1)$ simplex in Y^*, so that the quantities

$$\psi_j = \phi_j - \phi_m \tag{A2}$$

for $j=1,2,\ldots,m-1$ are linearly independent and a basis for Y^*. This assumption is typical of those always made in deriving the phase rule. Were the ψ's linearly dependent, this would imply an accidental and unexpected relationship among the f's. The essence of the phase rule is that such accidents do not occur.[19] We can, therefore, choose a basis y_k, $k=1,2,\ldots,m-1$, in Y such that

$$[\psi_j, y_k] = \delta_{jk}. \tag{A3}$$

Consequently, if

$$y = \sum_k^{m-1} t_k y_k, \tag{A4}$$

with the t's real numbers, we have

$$f_j(y) = -t_j + f_m(y), \tag{A5}$$

an equation which is also valid for $j=m$ if we adopt the convention

$$t_m = 0. \tag{A6}$$

The region in Y occupied by phase j is that in which $f_j < f_k$ for all $k \neq j$, or

$$t_j > t_k \tag{A7}$$

for all $k \neq j$. Similarly phases j and k coexist where f_j and f_k are identical and smaller than all other free energies, or

$$t_j = t_k > t_l \tag{A8}$$

for all $l \neq j$ or k. Similar expressions can be written down for coexistence of more phases than two.

One quickly verifies that the regions (A7), (A8), and their analogs are convex cones in Y. A different choice of f's leads to a different set of ψ's and thus a phase diagram related to the one just discussed by a nonsingular linear transformation [in the approximation represented by (A1)]. Thus all characteristic balls of m-phase coexistence are topologically equivalent.

APPENDIX B: CHARACTERISTIC BALLS AND GRAPHS FOR TWO COEXISTING ENTITIES

Let S and U be two (elementary or compound) entities with characteristic balls (Y, Q_Y) and (Z, Q_Z). Let X be the interval $-1<x<1$. Let $W = X \times Y \times Z$ consist of ordered triples[8]

$$w = (x, y, z), \tag{B1}$$

with x, y, and z in X, Y, and Z, respectively. The set $Q \subset W$ consists of (i) all w for which $x=0$, (ii)

all w for which $x<0$ and $y \in Q_Y$, and (iii) all w for which $x>0$ and $z \in Q_Z$.
The phase diagram (W, Q) is (we believe) topologically equivalent to the characteristic ball for SU. Should U be a one-phase point A, the above prescription must be modified so that $W = X \times Y$ consists of ordered pairs (x, y) and (iii) is to be ignored. An analogous modification occurs if $S = A$.

In order to obtain the characteristic graph of SU, it is convenient to first construct augmented characteristic graphs G_S and G_U for S and U by adding in each case an artificial "ghost" vertex at codimension -1 connected by edges to all vertices of codimension 0 (see Fig. 5). The augmented graph G_{SU} of SU has a vertex (s_j, u_k) for every vertex s_j in G_S and u_k in G_U with codimension given by

$$\kappa((s_j, u_k)) = \kappa(s_j) + \kappa(u_k) + 1 . \tag{B2}$$

There is an edge in G_{SU} between (s_i, u_k) and (s_j, u_l) if and only if either (i) $j = i$ and there is an edge in G_U between u_k and u_l, or (ii) $k = l$ and there is an edge in G_S between s_i and s_j.

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[1]The only higher-order critical points thus far observed in fluid mixtures are tricritical points. A number of references will be found in R. B. Griffiths and B. Widom, Phys. Rev. A 8, 2173 (1973).

[2]For some examples see R. B. Griffiths, Phys. Rev. B 7, 545 (1973); A. Aharony and A. D. Bruce, Phys. Rev. Lett. 33, 427 (1974).

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[7]R. Thom, in *Statistical Mechanics*, edited by S. A. Rice, K. F. Freed, and J. C. Light (University of Chicago Press, Chicago, 1972), p. 93.

[8]Addition and scalar multiplication defined by $(v, w) + (v', w') = (v + v', w + w')$; $a(v, w) = (av, aw)$. The dimension of $V \times W$ is the sum of the dimensions of V and W.

[9]J. E. Ricci, *The Phase Rule and Heterogeneous Equilibrium* (Van Nostrand, New York, 1951), p. 30; J. C. Wheeler, J. Chem. Phys. 61, 4474 (1974).

[10]By "free energy" we mean, for example, $-p$ as a function of T and the chemical potentials, or one of the chemical potentials as a function of p, T, and the remaining chemical potentials.

[11]If the boundary of Y is added to Q and the typical ball of a point on the boundary includes points outside of Y, it will presumably be topologically equivalent to SA or the cylinder of SA, which is the motivation for the symbol Sa.

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[16]J. P. Straley and M. E. Fisher, J. Phys. A 6, 1310 (1973).

[17]R. J. Baxter, J. Phys. C 6, L445 (1973).

[18]The physical interpretation of the ϕ's is that they are points in a space of thermodynamic densities (see Ref. 3), for example, the number of particles per unit volume of each species and the entropy per unit volume.

[19]I am indebted to Dr. J. C. Wheeler for this comment.