

Tricritical points in multicomponent fluid mixtures*

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In view of experimental considerations, we give a model-independent argument that the novel tricritical points in multicomponent fluid mixtures, where three phases simultaneously become critical, are points on the boundary of a *single two-dimensional surface of critical points*. This result is corroborated by the Landau model suggested by Griffiths. The relationship between these tricritical points and the complex "higher-order" critical points proposed to exist in certain magnetic systems is elucidated.

I. INTRODUCTION

In 1970 Griffiths¹ proposed the concept of a tricritical point as being the point of intersection of three lines of critical points in a phase diagram using intensive thermodynamic variables. He further suggested, as examples, metamagnets,² He³-He⁴ mixtures,³ and ammonium chloride.⁴ There has also been considerable speculation^{1,5} that similar points might exist and might be found in the phase diagrams of complex fluid mixtures. That such points have already been proposed and, indeed, that they had been investigated prior to 1970 has recently been pointed out by Widom and Griffiths.⁶⁻⁸ A full and very complete discussion of experimental evidence for these points has been given in Refs. 6-8, and we refer the reader to these papers for details.

A different way in which critical points more complex than tricritical points can occur has been shown to involve intersecting lines of tricritical points, and a classification of critical points has been introduced to differentiate these points from tricritical points or ordinary critical points.⁵ The question has been raised^{6,8} as to how the new points discovered in fluids are related to such a classification.

Properties of the phase diagram⁹ were the basis of the approach we suggested previously.^{5,10} In particular, we emphasized the importance of the connectivity properties of different spaces of critical points and tricritical points. Accordingly it is the connectivity of the different critical points of multicomponent fluid mixtures in the space of truly intensive or "field" variables that we emphasize here.

II. DEMONSTRATION THAT ALL CRITICAL POINTS FORM A SINGLE CONNECTED SURFACE

The basic idea is to consider a system where three distinct phases can be in equilibrium. These might be three liquids or two liquids and a vapor phase. On changing the thermodynamic variables (temperature, pressure, chemical potentials of different components) one pair of phases will become critical, in the presence of the third. In a binary system the point where this occurs is the end point of a line of critical points which bounds the surface of points where the two phases coexist. There are no degrees of freedom and such a point is unique in the phase diagram.⁷

In a ternary, quaternary, or more complicated system this point has one or more degrees of freedom. Thus a line of "critical end points" is possible. Such a line is the boundary of a surface of critical points where two phases are critical.

In the particular systems of interest it is possible, by varying physical conditions, to make a different pair of the three phases become critical in the presence of the third, thus producing a second line of critical end points.

Finally, by achieving exactly the correct physical conditions it is possible for all three phases to become critical simultaneously. In a ternary system such a point is unique; there are zero degrees of freedom. Here, only this and similarly simple cases are considered.

Experimentally there is the following arrangement. A tube containing a three-component mixture with a three-phase system is cooled to observe the appearance of successive phases. We

will call these phases α , β , and γ , where for purposes of argument $\rho_\alpha < \rho_\beta < \rho_\gamma$. The ratio of the various components is varied until the second meniscus appears via a critical mode. This could be the lower meniscus in which case phases γ and β become critical at a lower temperature. If pressure, temperature, and one other intensive parameter are allowed to vary, a phase diagram of the type shown in Fig. 1(a) will be observed. At the point P , the phases γ and β become critical in the presence of a third phase α . If pressure is increased, the lightest phase α will disappear and a line of critical points between phases γ and β will develop. For increasing temperatures above P , there will be a line of critical points bounding the surface of coexistence points which separates the region of light phase α from the region of the heavier phase $\gamma\beta$.

By varying the ratios of components appropriately, it is possible, in the physical systems of interest, to make the upper meniscus, separating phase β from phase α , appear second on cooling. The corresponding phase diagram is shown in Fig. 1(c). Again there is a special point P' which is the end point of a line of critical points for phases β and α , and which is also the end point of the line of points where three phases coexist. If the temperature is increased above P' then the coexistence surface separating phase γ from the

combined phases $\beta\alpha$ will terminate in a line of critical points.

If the transition to the phase diagram of Fig. 1(c) happens by a continuous variation from Fig. 1(a) then there must be a situation where both menisci become critical simultaneously.

The corresponding phase diagram is shown in Fig. 1(b). It may be seen that the point P of Fig. 1(a) has migrated along the coexistence surface to the point P_t on the boundary. At the point P_t all three lines of critical points, a ($\gamma\beta$ critical), b ($\gamma\alpha$ critical), and c ($\beta\alpha$ critical) meet.

The purpose of constructing Figs. 1(a)–1(c) is to consider the behavior of the critical surface in the immediate neighborhood of the tricritical point P_t , and the figures should therefore be understood to represent the phase diagram close to P_t and not far away from the tricritical point. Also, since our primary interest is the connectivity of the surface of critical points, and not its specific shape, we do not have to choose the variables precisely, since the connectedness would remain unchanged even if different variables were chosen. [Similar remarks apply to Figs. 2(a) and 2(b) in what follows.]

We can now demonstrate that the lines of critical points a, b, c in Figs. 1(a)–1(c) form a single continuous surface of critical points bounded by the line of critical end points P – P_t – P' . Consider a

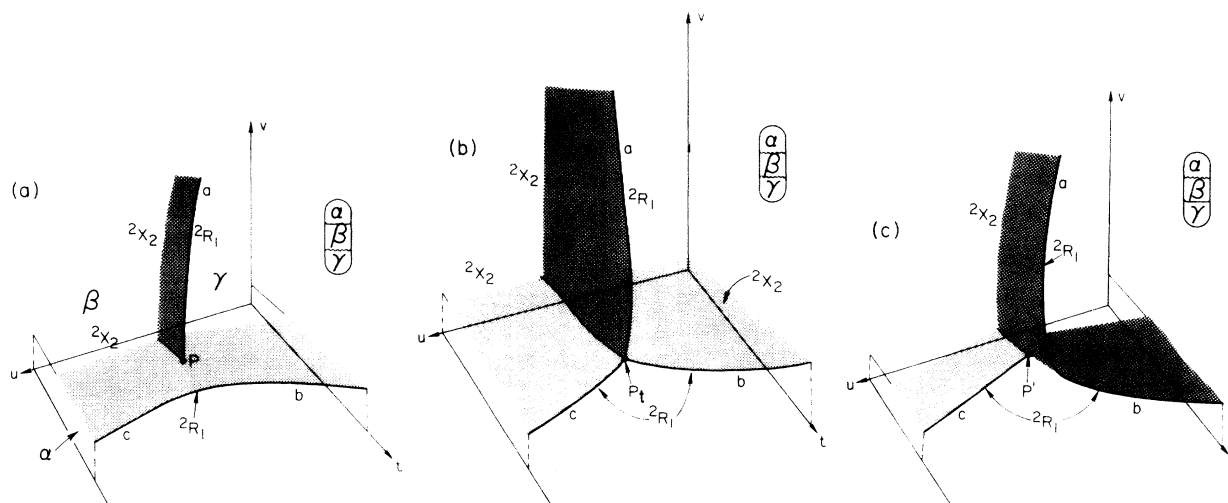


FIG. 1. Three-dimensional subspaces of the full four-dimensional space of field variables of a three-component system (or of five dimensions for four components). The variable t may be thought of as the temperature, the variable v as the pressure, and the third variable u as a suitable combination of chemical potentials. We use the notation of Ref. 5 to indicate lines and surfaces of critical points in the diagram. Lines of critical points are indicated 2R_1 (order 2, dimension 1). Coexistence surfaces are indicated by 2X_2 (two phases and dimension 2). (a) Section containing a point P where the two heavier phases γ, β are critical in the presence of the lightest α , as represented by the schematic tube showing the $\gamma\beta$ meniscus critical and the $\beta\alpha$ meniscus stable. (b) Section through the point P_t where all three phases become critical simultaneously, the $\gamma\beta$ and $\beta\alpha$ menisci are simultaneously critical in the schematic tube. (c) Section containing a point P' where the lighter phases β, α are critical in the presence of the heaviest γ , as shown in the schematic representation.

point on line a in Fig. 1(a); move continuously through Figs. 1(b) to 1(c). Now move along the line a - b to a point at the "b" end, and now move along continuously through Figs. 1(b) to 1(a). Still being on line b , we can move along the line b - c to the "c" end. Now move continuously through Figs. 1(b) to 1(c) and our assertion is demonstrated. We have not passed through the point P_t and so the lines a, b, c form sections of a single continuous surface of critical points bounded by lines of critical end points $P-P_t-P'$.

The fact that there is only a single surface of critical points is also corroborated by the model of Griffiths⁸ (see his Fig. 3). This fact is in strong contrast to the metamagnet where it is not possible to go from a point on the wing boundaries to a point on the physical critical line without passing through a tricritical point^{1,10} and the spaces of critical points are distinct and separate.

It will be plausible to conjecture that since all the critical points form a single surface, the critical-point exponents are the same at all critical points except the tricritical point itself. In contrast, for a metamagnet no reasons have been presented for why the critical-point exponents should be the same along all three of the critical lines meeting at the tricritical point. However, it has been suggested¹¹ that for most tricritical points the existence of a hidden variable linking the wing boundaries to the physical critical line (the variable called a_3 by Griffiths⁸) might force the equality of exponents.

III. MODEL SURFACE OF CRITICAL POINTS

The phase diagrams of Figs. 1(a)-1(c) were three dimensional and so parametrizing them with an extra field variable introduces a fourth dimension to the phase diagram. The connectivity, and other properties, of the surface of critical points formed by the critical lines a, b, c of Fig. 1, are most easily studied in a three-dimensional subspace of the full phase diagram which contains the whole critical surface. The shape of the critical surface in such a subspace may be determined as follows.

Consider the critical lines as they appear on the paper in Figs. 1(a)-1(c) and consider how these lines would form a smooth surface in three dimensions if the extra parameter were used to plot the height of the paper, with Fig. 1(c) above 1(b) above 1(a). By this combined projection and motion we generate a single connected surface of critical points with a boundary formed by the line of points $P-P_t-P'$.

A surface, which is topologically equivalent to the surface of critical points thus obtained, is

shown in Figs. 2(a) and 2(b). Fig. 2(a) is a contour map of the surface, and the heights h of the contours are given by the hyperbolae $xy = h$. The boundary of the surface $P-P_t-P'$ is represented by the parabola $y = -cx^2$ in the lower half of Fig. 2(a). The topological equivalence of the surface of Fig. 2(a) to the surface of critical points may be seen as follows.

Consider a section of Fig. 2(a) at constant height h . If $h > 0$ there are two hyperbolae, one in the upper right quadrant and one which terminates on the portion of the parabola labeled P in the lower left. This is a representation of Fig. 1(a) for which there are two critical lines, one labeled (a) terminating at P and another labeled (b - c).

If $h < 0$ there are again two hyperbolae, one in the upper left quadrant which corresponds to the line of critical points (a, b) of Fig. 1(c), and one

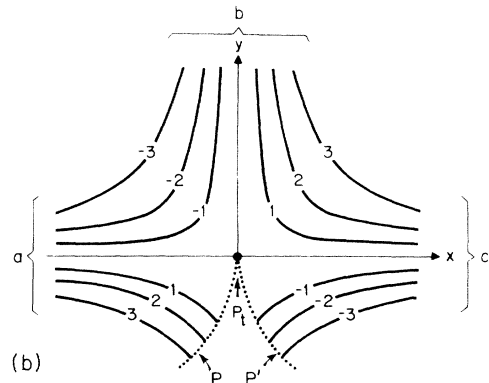
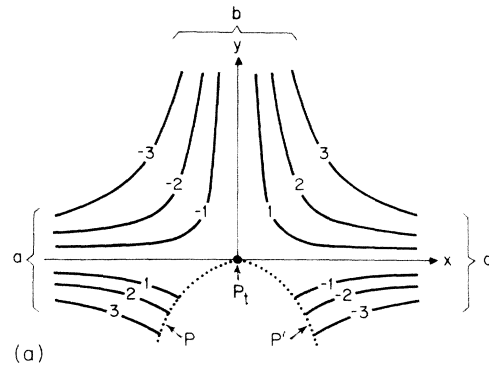


FIG. 2. Section of the four-dimensional space of field variables containing the full surface of critical points. The surface is represented by a contour map of hyperbolae and is fully explained in the text. The variables x and y are suitable field variables. (a) Boundary of the surface is smooth at P_t . The lines of critical end points P, P' form a smooth line in the four-dimensional space. (b) Boundary of the surface is cusplike at P_t . The lines of critical end points P, P' form a cusp in the four-dimensional space.

in the lower right quadrant of Fig. 2 which corresponds to the critical line c terminating at P in Fig. 1(c).

When $h=0$ the hyperbolae degenerate into the three axes, for $x<0$, $y>0$, and $x>0$ corresponding to the lines a, b, c of Fig. 1(b) which terminate at P_t .

Accordingly, in Fig. 2, the ends of the hyperbolae are labeled a, b, c according to the parts of the critical lines in Fig. 1 to which they correspond.

The complete topological correspondence between the sections of the surface in Fig. 2 and the critical lines of Fig. 1 is therefore clear. The points P, P_t, P' are a line forming a boundary of the surface of critical points, and the point P_t , which is the tricritical point, corresponds to a saddle point of the surface in the projective space of Fig. 2.

It may seem that a very special space has been chosen, and that the boundary has been made to go in a very special fashion—through the saddle point. However, this is merely in accordance with the following general physical requirements: (i) Only one point P occurs in each phase diagram; therefore the boundary *has* to pass from the lower left quadrant to the lower right quadrant without passing through the upper two quadrants; (ii) Critical lines only split or end at a point like P . Thus the point P *has* to pass through the origin where the section would otherwise necessarily give four lines of critical points intersecting.

This analysis of the critical points as a single surface provides another viewpoint from which to understand the fact that only two pairs of the three possible pairs of phases became critical in the presence of the third. The simplest viewpoint is that of the test tube itself. If the phases α, β, γ are ordered in increasing density, then (α, β) can be critical (same density) in the presence of γ , and $(\beta\gamma)$ can be critical in the presence of α , but $(\alpha\gamma)$ cannot be critical and of equal density without the phase β having a density equal to both. Thus the possibility $(\alpha\gamma)$ critical in the presence of β is eliminated. Widom⁷ has related this fact to the geometric asymmetry of the solid figure containing three distinct phases α, β, γ at constant temperature less than the tricritical temperature.

In terms of the phase diagrams in spaces of truly intensive variables (Widom used densities, or extensive variables), the existence of two lines of critical end points instead of three has a very simple topological interpretation: the boundary of a single surface is locally divided into *two* separate parts by the removal of a single point. Thus the tricritical point P_t divides the boundary of the surface of critical points into two lines of critical

end points but *cannot* divide it into three different lines of critical end points.

IV. SPECIAL DIRECTIONS

It was shown by Griffiths⁸ that in his model there are four variables of scaling, each with different exponents at the special point. From a purely phenomenological point of view one can define four different directions at the special point P_t in the same spirit as Griffiths and Wheeler.⁹ From Fig. 2 it may be seen that these directions are (i) the limiting "strong" direction for the surface of critical points, (ii) the limiting "weak" direction for the surface of critical points, (iii) the tangent to the line of critical end points at the tricritical point, and (iv) the limiting second direction parametrizing the surface of critical points. These correspond to the variables called a_1, a_2, a_4 , and a_3 , respectively, by Griffiths.⁸

V. TRANSLATION TO COMPOSITION VARIABLES

The variables over which the experimentalist has easy control are unfortunately not the intensive field variables like the chemical potentials, but only the densities. In these variables the phase diagrams have been discussed by Widom.⁷ It has been pointed out by Griffiths⁸ that the precise composition of the tricritical point P_t probably does not coincide with the composition of the regions of coexistence of three phases at temperatures smaller than the temperature at P_t .

Such behavior has probably been observed in the system carbon-dioxide-methanol-water because when a constant volume specimen (i.e., a sealed tube) of precisely the correct composition is increased in temperature, one does not observe the simultaneous disappearance of two menisci. Instead¹² one meniscus disappears critically and simultaneously a second appears critically. This remarkable behavior does not change any of our geometric conclusions, because it can be interpreted as follows: the constant volume, constant composition path does not follow the line of points where three phases coexist in Fig. 1(b), but rather it passes from one coexistence surface (γ, β) to another (α, β) directly through the point P_t .

VI. RELATIONSHIP TO OTHER COMPLEX SYSTEMS

In previous work^{5,10} we have given several examples of complex magnetic systems and we have attempted to systematically classify all the coexistence and critical points in such systems. For

points where several phases coexist without being critical this is relatively simple, since the appropriate quantities are the number of coexisting phases and the dimensionality of the space. These are related to the total number of thermodynamic intensive variables by the phase rule.⁵

For critical points, it can be argued that every phase that becomes critical after the first two implies the loss of an extra degree of freedom in addition to the one lost because of coexistence.⁷ Hence if there is a system with n thermodynamic variables possessing a point where p phases are in coexistence, of which q are critical (altogether rather than in two separate groups q_1 and q_2 , although the generalization to such cases is simple). The dimensionality of the space on which this occurs will be given by

$$d = n - (p - 1) - m, \quad (1)$$

where $m = \max(q - 1, 0)$ since the case $q = 1$ is not meaningful and $m = 0$ if $q = 0$. As a special case if all p of the phases are critical we obtain $d = n + 2 - 2p$.

While this equation holds for fluids, it is violated by the original tricritical points, for which $n = p = 3$, $d = 0$ and also by certain magnetic models¹⁰ which contain highly symmetric points where lines of tricritical points intersect, and $n = p = 4$ and $d = 0$. Before giving the equation which correctly describes both fluids and the complex magnetic systems let us contrast the two ways of classifying more complicated critical points that have been proposed.

For fluids Widom⁷ has proposed that the important quantity is the number of phases becoming critical, and that this number should be used as the order of the critical points.

For complex magnetic systems we have proposed an apparently different scheme which is based on the original proposal for tricritical points¹ where three different lines of critical points intersected. Accordingly we gave examples of systems where different lines of tricritical points intersected, and gave the points of intersection an order different from (one larger than) that of tricritical points. Because of the symmetry of the various systems we investigated, there were no lines of critical end points, i.e., points where one or more phases coexist with others that are critical. Consequently the number of variables n needed to obtain a point where four phases are simultaneously critical was reduced from six to four.

For tricritical points in fluids, it is possible to artificially reduce the number of variables and eliminate the lines of critical end points from the phase diagram. For example, Fig. 1(b) is an illustration of this since it is a three-dimensional

section of the four-dimensional field space with all lines of critical points ending at the tricritical point. Similarly the $h = 0$ section of Fig. 2 produces the same result. Griffiths⁸ has shown how a similar phase diagram can be obtained by taking the section $a_3 = 0$ of his four-dimensional phase diagram with variables a_1, a_2, a_3, a_4 .

Let us now return to the case of the intersecting lines of tricritical points in the variable interaction metamagnet. It has been shown¹⁰ that the point of intersection (the point of order 4) is a point where four phases become simultaneously critical. Thus in this case the definition of order suggested by us coincides with the definition suggested by Widom.⁷ This fact may be generalized, because the only reason there should be more than one line of tricritical points is because there are more than three phases available. The different lines of tricritical points will intersect at points where more than three phases become simultaneously critical.

To obtain a version of Eq. (1) which is satisfied by all the cases considered so far, it is necessary to consider the number of variables which possess nonzero scaling power at the point under consideration. It is important to note that this number may be less than the number of significant directions picked out by the phase diagram. For example, on an ordinary line of critical points three directions are determined, but only two (the strong and weak) are associated with variables which scale. Alternatively, on the line of critical end points P, P_t, P' , all four of the directions (i)-(iv) are defined but only (i) and (ii) are associated with variables which scale (except at P_t where all four enter the scaling equation). The implications of the simple Landau model⁸ are that for fluids the number of scaling directions $s = 2(q - 1)$. Another quantity that is important is the number of phases which are in equilibrium but which are not critical, $x = p - q$. In terms of the variables s and x , Eq. (1) may be rewritten as¹³

$$s + x + d = n. \quad (2)$$

It will be seen that this equation also holds for the old tricritical points, and the intersection of lines of tricritical points. It is satisfied by construction from (1) by all the points in generalizations of Widom's scheme for which the order is given by $\Theta = q = \frac{1}{2}s + 1$ and by all the points in our scheme⁵ for which the order is given by $\Theta = s$. These two possibilities express, respectively, the maximum and minimum number of scaling variables at a point where Θ phases became critical, $\Theta \leq s \leq 2(\Theta - 1)$. For $\Theta = 2$ there is only one possibility, $s = 2$; for $\Theta = 3$ there are two cases, $s = 3, 4$; and for $\Theta > 3$ there are many possibilities.

Thus we have proposed⁵ a minimal scheme for complex critical points whereas Widom and Griffiths have proposed a maximal scheme.

In conclusion it should be reiterated that while the definition of order for critical points suggested in Ref. 5 does not appear to be applicable to fluids, it is consistent with the definition in terms of the number of phases becoming critical.⁷

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¹³We are much indebted to J. Nicoll for discussions leading to this equation. A more complete account will be given in a separate paper.

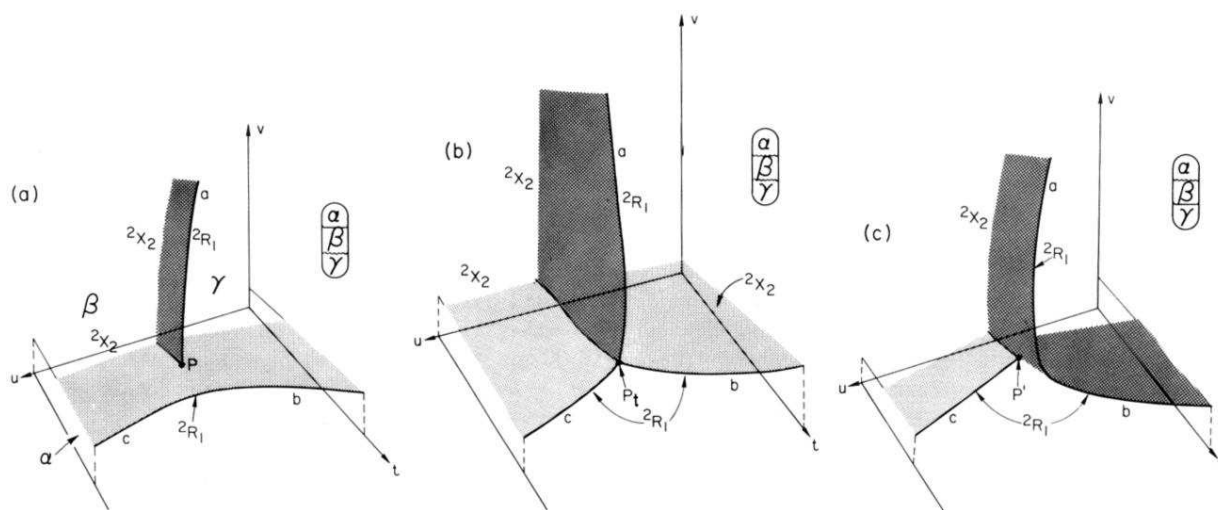


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