SLAC-PUB-1259
June 1973

TRICRITICAL POINTS IN MULTICOMPONENT FLUID MIXTURES: A GEOMETRIC INTERPRETATION*

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ABSTRACT

We consider special critical points in multicomponent fluid mixtures, where critical phenomena occur between three phases simultaneously. We show that although such points may be the intersection of three lines of critical points, they are not in general analogous to the tricritical points originally proposed by Griffiths. Rather the three lines are part of a single surface of critical points and the special point occurs where the boundary of the surface of critical points is a maximum with respect to a particular variable selected experimentally (usually temperature). We suggest experimental tests to determine whether the boundary is singular at the point, making it also a special point. Finally, we relate the entire discussion to the recently proposed concept of order for critical points and discuss the possibilities of special scaling.

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[*] Supported in part by the U.S. Atomic Energy Commission.

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[§] Supported by NSF Grant No. GU-1590 and NASA Grant No. NGL 34-002-084. Permanent address: Riddich Laboratories, North Carolina State University, Raleigh, North Carolina 27607.

[¶] Supported by NSF Grant No. GP-15428.

(Submitted to Phys. Rev. A)

I. INTRODUCTION

In 1970 Griffiths[1] 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], He^3 - He^4 mixtures[3], and ammonium chloride[4]. There has also been considerable speculation that similar points might exist and might be found in the phase diagrams of complex fluid mixtures. In fact, following a suggestion by Kohnstamm[5], situations where two phase boundaries become critical simultaneously have been observed by Radyshevskaya[6], Krichevshii[7], Efremova[8,9,10] and their co-workers[11]. In such cases, a particular phase diagram may contain a point where three lines of critical points intersect, and which therefore is apparently a tricritical point.

In this work we analyse, in Section II, a typical sequence of phase diagrams for complex fluid systems, one of which shows a tricritical point. We show that the lines of critical points generate <u>a single connected surface of critical points.</u> In contrast, in the examples given by Griffiths, there are definitely three definite and distinct lines (or higher dimensional spaces) of critical points, and it is impossible to pass from one line (or space) of critical points to another without passing through a tricritical point.

We therefore suggest that the special points found in the phase diagrams of multicomponent fluid systems as exemplified by the example given in Section II are best understood <u>not</u> as points with special critical properties, like a tricritical point,[12,13,14] but simply as a point on the boundary of a surface of critical points, where the boundary bears some special geometric relation to the thermodynamic axes. Thus the special point is more analogous to a critical azeotrope, as discussed by Griffiths and Wheeler[15], rather than to a tricritical point[1].

In Section III we propose a model surface in a three dimensional space which exactly mimics the shape of the real surface of critical points in the full four dimensional space of field variables.

In Section IV we relate the model surface to the experimental results and show that it enables one to understand all the behaviour discovered so far in terms of the geometry of the line of critical end points (i. e. the boundary of the surface of critical points). In particular, we show that the line of critical end points passes through a temperature maximum.

In Section V we relate the ideas to the concept of order[16] of critical points and also to the possibility of special scaling at the special point.

II. PHASE DIAGRAMS FOR MULTICOMPONENT FLUID MIXTURES

Several different experimental arrangements[6-11] have been used to observe complex critical points in fluid mixtures. They are all variations on the simple theme originally proposed[5], so we will analyse the phase diagram for the fundamental experiment first and consider in detail the relationships and similarities between this experimental situation and the others in Section IV below.

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 vapour 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 this point 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.

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. In this paper, only this and similarly simple cases are considered.

Experimentally one has the following kind of 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 A, B, C where for purposes of argument $\rho_A > \rho_B > \rho_C$. 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 A and B 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 Figure (1a) will be observed. At the point P, the phases A and B become critical in the presence of a third phase C. If pressure is increased, the lightest phase C will disappear and a line of critical points between phases A and B will develop. P is the end point of this line of critical points. For increasing temperatures above P, there will be a line of critical points bounding the surface of critical points which separates the region of light phase C from the region of the heavier phase AB.

By varying the ratios of components appropriately, it is possible, in the physical systems of interest, to make the upper meniscus, separating phase B from phase C, appear second on cooling. The corresponding phase diagram is shown in Figure (1c). Again there is a special point P'' which is the end point of a line of critical points for phases B and C, 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 A from the combined phases BC will terminate in a line of critical points.

If the transition to the phase diagram of Figure (1c) happens by a continuous variation from Figure (1a) then there must be a situation where both menisci become critical simultaneously. This was the situation postulated by Konstamm[5] and the corresponding phase diagram is shown in Figure (1b). It may be seen that the point P of Figure (1a) has migrated along coexistence surface to the point P' on the boundary. At the point P' all three lines of critical points, a (AB critical), b(AC critical), and c (BC critical) meet.

These considerations show that the point P' where the two menisci become critical simultaneously is a tricritical point. However, it is a tricritical point of a very different nature from those originally proposed by Griffiths[1] (see introduction), as is demonstrated by the following assertion: "The lines of critical points a, b, c in Figures 1(a-c) form single continuous surface of critical points bounded by the line of critical end points P, P', P". In fact it is possible to go from a point on the line a in Figures (1a) or (1b) to a point on the line c in Figures (1b) or (1c) without ever passing through the point P'."

In contrast, in a metamagnet, it is never possible to go from a point on the wing boundaries to a point on the physical critical line without passing through a tricritical point, and this shows that the systems should not necessarily be considered related as far as properties of the special point are concerned.

To demonstrate the above assertion, consider a point on line a in Figure (1a); move continuously through Figure (1b) to Figure (1c). Now move along the line a-b to a point at the "b" end. Now move back continuously through Figure (1b) to Figure (1a). Still being on line b, we can move along the line b-c to the "c" end. Now move continuously through Figure (1b) to Figure (1c) and our assertion is demonstrated. We have not passed through the point P' and so the lines a, b, c form sections of a single continuous surface. A model for this surface is considered in the next section.

III. A MODEL FOR THE CRITICAL SURFACE AND ITS BOUNDARY

The phase diagrams of Figures (1a, b, 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 Figure 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 Figures (1a, b, 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 Figure (1c) above Figure (1b) above Figure (1a). 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', P''.

A surface which is topologically equivalent to the surface of critical points thus obtained is shown in Figure 2. Figure 2 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', P'' is represented by the parabola $y = -cx^2$ in the lower half of Figure 2. The topological equivalence of the surface of Figure 2 to the surface of critical points may be seen as follows:

Consider a section of Figure 2 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 labelled P in the lower left. This is a representation of Figure (1a) for which there are two critical lines, one labelled 'a' terminating at P and another labelled (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 Figure (1c), and one in the lower right quadrant of Figure 2 which corresponds to the critical line c terminating at P'' in Figure (1c).

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 Figure (1b) which terminate at P'.

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

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

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 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.

One question that is open is whether the boundary passes smoothly through the origin as indicated in Figure 2, or whether the lines P and P'' in Figure 2 intersect at a finite angle. This can be decided experimentally by tracing out the line of points P, P', P'' in the four dimensional space and seeing if it is smooth. Any projection of the line can also be plotted provided that the direction of projection is not tangent to the line at the point P'.[17]

If the line P, P', P'' is smooth, the non-uniqueness of the point P' is entirely self-consistent. This can be seen by considering Figure 2; if a different physical variable had been held constant, then one would be choosing cross sections of the surface that were not horizontal, but were a family of surfaces one of which was tangent to the critical surface, not at P' but at a different point on P or P''. The new point of tangency would correspond to a different point in the full four dimensional field space. Therefore the apparent tricritical point would be a completely different point on the line P, P', P''.

In such cases, the tricritical point[1] is not unique, but depends entirely on the choice of variable that is held constant to obtain the phase diagrams Figure (1a, b, c). Under these circumstances, calling P' a special "tricritical point" only serves to obscure the reality of the situation.

This is the situation which we suggest holds experimentally: that no unique tricritical point has been found, but that the boundary of the surface of critical points has assumed a special orientation. In the artificial example of Figure 2 the boundary passed through a saddle point and a maximum of the variable y. In the next section different special orientations will be demonstrated.

It is still possible for the point P' to be unique. For instance, if the line of points $[P, P', P'']$ is not smooth at P' (as mentioned in Section II) then P' is a special point.

There is a second way in which P' could be special, and that is if the critical surface developed a singularity there. In that case the boundary would not be smooth either, so this second case implies the first but not vice-versa. The way to tell if the critical surface is smooth at P' is to determine whether the three critical lines a, b, c meeting at P' are coplanar. If they are coplanar then the surface can be smooth, whereas if they are not it cannot possibly be.

The analysis in terms of a saddle point suggests that the lines a and c join smoothly at P', but while this is also possible it could be the result of the projection. Thus the coplanarity of a, b, c at P' (which is a weaker condition than colinearity of a, c at P') is a better test of smoothness of the surface of critical points.

If either of these two cases is true then the tricritical point P' is indeed a special point, but otherwise P' is a point on a smooth boundary of a smooth surface and should have no special properties. The implications of this for scaling are discussed in Section V.

IV. RELATION TO EXPERIMENT

Here we relate the analysis of the two previous sections to the various experiments that have been performed on multicomponent fluid mixtures.[6-11] All these experiments locate the boundaries of a region where three phases coexist and look for special critical points thereon. Systems of at least three components are used, for reasons explained in Section II, and the constant pressure, constant temperature phase diagram data have been reported in terms of the relative proportions of the three or four components, i. e. in terms of the usual triangle or tetrahedral phase diagram. It is easy to make a qualitative translation from these phase diagrams to the form in terms of intensive field variables (relative chemical potentials of the components) which Griffiths and Wheeler[15] suggested were more useful for the study of critical phenomena. However, the latter are more difficult to determine experimentally than the usual phase diagrams.

The first system to be investigated specifically to look for the phenomenom of the simultaneous appearance of two menisci by a critical mode was the system butane, water, acetic acid.[7] Between the temperatures 152° and 185° there are two critical points possible, one between two lighter phases in the presence of a heavier "liquid" and another between two heavier phases in the presence of a lighter "gas." As the temperature approaches 185° the compositions of the phases involved at the different critical modes approach each other and above 185° it is no longer possible to have three different phases in equilibrium. This was interpreted[7,8] as being a point where two different lines of critical end points intersected. From our point of view we propose that this should be regarded as a point where a single line of critical end points passes through a temperature maximum; i. e. a tangent to the curve at the special point is perpendicular to the temperature axis. This is in qualitative agreement with the experimental data[7]; it is also indicated by the extremely rapid variation in composition of the critical end points near the special point.

A corollary of this interpretation is that the liquid, liquid critical phenomena, are very similar to the liquid gas critical phenomena (i. e. same exponents) since they are part of the same surface of critical points.

A system similar to the one just described is carbon dioxide, methanol, water.[8,9] Here again there are two critical end points at the same temperature which approach one another as the temperature is increased to 45°C. Above this temperature there are no compositions where the three phases may be found in equilibrium. We again interpret the special point as a point where a single line of critical end points passes through a temperature maximum.

For the system carbon dioxide, methanol, water the larger number of phase diagrams provided (Figures 1,2,3 of reference 9) enables one to see clearly that the various lines of critical points do indeed form a single connected surface, and this provides confirmation of the arguments of Section II. In terms of the model surface, Figure 2 of Section III, we have chosen the variable y as the temperature. For $y < 0$ ($T < T_{special}$) the surface of critical points is cut into two disconnected lines ending at two different critical end points which in turn are joined by a line of points where three phases coexist (c. f. Figure 2 of reference 9) and for $y > 0$ ($T > T_{special}$) there is a single line of critical points. When all are combined there is only a single surface of critical points with a continuous boundary.

Another aspect of the system carbon dioxide, methanol, water, which deserves comment is that 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. Instead[9] one meniscus disappears critically and simultaneously a second appears critically. This remarkable behaviour 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 Figure (1b). Instead it passes from one coexistence surface (A, B) to another (B, C) directly through the point P'.

The other class of systems where the special points have been observed are four component systems.[6] Here the phase diagrams make it clear from the start that there is only one surface of critical points and that there is an extremum beyond which the system does not exhibit three phases but only two. Thus the special point is again an extremum on a line of points where three phases coexist. Experimentally a temperature maximum was observed for the existence of three phases in the system ammonium sulphate, water, ethanol, benzene. In this kind of experiment the role of the fourth component is to obviate the need to vary the pressure[1], making experimental apparatus and procedures much simpler. If the pressure was also varied in this or similar systems, even more interesting critical behaviour could conceivably be found.

V. ORDER AND SCALING

In this section we are concerned with the order of the critical points discussed in the last three sections, and also with the related property of scaling.

Order of spaces of critical points[16] was introduced to classify spaces of critical points in complex magnetic systems. Specifically, the order of a particular space of critical points was defined to be one more than the order of the spaces of critical points which intersected these, and ordinary critical points were defined to be of order $\mathcal{O} = 2$. Thus a tricritical point is of order $\mathcal{O} = 3$. In the examples given in reference 16 the points of order 3 are stable under changes of a parameter: thus the tricritical point remains a tricritical point; for He^3, He^4 mixtures as the pressure is changed, and in metamagnets as the interplanar interaction strength is varied. In one example, the model analysed by Nagle and Bonner, the tetracritical point (where four lines of critical points intersect) splits into two tricritical points as a parameter is varied; it was pointed out that the tetracritical point is a point on a smooth line of tricritical points and arises because a hypersurface of the full four dimensional space which is tangent to the line of tricritical points has been chosen. Thus the special "tetracritical" point arises because of a special geometry and not from any intrinsic special properties of the point. Indeed by taking different hypersurfaces, of the four dimensional space, any other point on the line of tricritical points could be made to appear a tetracritical point.

A similar case is occurring here: under the variation of a parameter the tricritical point is splitting, in such a way that all the critical lines form a single surface, Figures (1a, 1c) as opposed to Figure (1b). Further if the point P' is a point on the smooth boundary of a smooth surface, as suggested in Sections III and IV, then different points on the boundary could also be made tricritical points by choosing different thermodynamic variables to be constant. Since P' is never the point of intersection of different spaces of critical points of order two, but is merely the point of intersection of different subspaces of a single space of critical points, it should not be classified as a critical point of order three. Rather it should be described as a point on the boundary of a space of critical points of order two, and whether it is associated with a singularity of the boundary (and is therefore a special point) must be determined experimentally.

One way that a critical point of order three could develop in these systems would be if the sequence of phase diagrams was Figure (1a), Figure (1b) and back to Figure (1a) again. The point P migrating to the boundary of the coexistence surface and then back on the same surface. Here the line of critical points a would form a distinct critical surface different from that swept by the line of points b, c. The two distinct critical surfaces would intersect at P' which would therefore be a critical point of order three.[18] Note that usually there are three different spaces of critical points intersecting at critical points of order three but here there would only be two.

The definition of order of a critical point depends only on the phase diagram. However it has recently been shown that scaling laws may be valid at all spaces of critical points because of the existence of fixed points of the renormalisation group in the space of all Hamiltonians. If order is a fundamental property of spaces of critical points it should be related to properties of critical spaces dedeuced from the renormalisation group approach.

In all the examples known to the authors, and as proposed in reference 16, the order of a critical point is equal to the number of relevant scaling field variables. If this is taken as an alternative definition of order, then one has a separate criterion to classify the order of the point P'.

If P' is a special point of the surface and/or the boundary, there may be an extra scaling hypothesis valid at P' and no where else. It may possibly be an isolated critical point of order three. If, however, P' is a point on the smooth boundary of a smooth surface of critical points, there should be no special scaling hypothesis valid at P' unless one is also valid at P and P'', then the whole boundary could possibly be of order 3. This is a very interesting experimental question, and suggests that investigation of the scaling exponents on the critical surface and at the boundary of the critical surface of experimental systems would be worthwhile.

VI. CONCLUSION

We have shown that for the class of experimental systems considered, the lines of critical points form a single continuous surface, and that the special points suggested by Kohnstamm and found experimentally are probably points where the boundary of the surface of critical points has a special orientation with respect to the thermodynamic variable axes.

The universality hypothesis implies that critical point exponents are the same at every point of the surface and we conclude that surprisingly, there are not necessarily any special critical properties at the special points, analogous to those at the tricritical points.[1-4, 12-14]

Secondly, we have suggested experimental measurements that would decide whether the tricritical point P' was really a point on the boundary of a smooth surface or whether the surface and/or the boundary possesses a singularity there. If both the boundary and the surface are smooth, as was the case for the particular model given in Figure 2, any special property of the point P' should be a property of the whole boundary (P, P', P"). If the scaling exponents were found to be different at P', then in this case they should be different for the whole boundary.

Alternatively, failure to find special scaling at the point P' should not be taken to indicate the failure of scaling at tricritical points in general, but only that one should be very careful to consider at which critical points to investigate the validity of special scaling hypotheses. In particular the tricritical point should be a genuine critical point of order 3, that is to say, it should be stable under small variations of a parameter instead of degenerating into different end points P and P".

ACKNOWLEDGEMENT

We wish to thank Professor R. B. Griffiths for a most stimulating conversation.

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17. In concrete terms this means that temperature should not be included in the variables used to plot the position of point P.
18. Note that Eq. (1.1) of reference 16, I would be satisfied as an inequality.

FIGURE CAPTIONS

Figure 1 Phase diagrams exibiting an end point of a line of critical points where two phases are critical in the presence of a third. The axis t is temperature, while v, u are pressure and a chemical potential. Three phases A, B, C exist in the regions indicated and coexist on the various surfaces, labelled ${}^2X_2$ in the notation of reference 16. The coexistence surfaces are bounded by lines of critical points a, b, c labelled ${}^2R_1$, also in the notation of reference 16.

(a) The line of critical points a ends at P.

(b) The lines a, b, c end at a "tricritical point" P'.

(c) The line c ends at the point P".

Figure 2 A contour map of a model surface equivalent to the surface of critical points of Figures (1a, b, c). Experimentally the variable y is temperature.