Tricritical Point in Four-Component Fluid Mixture

Ikuo SUZUKI

Department of Engineering Sciences

(Received August 25, 1983)

A brief historical account of studies of higher order critical points in multicomponent fluids is given. Most of the paper is devoted to a review of the theoretical model given by Griffiths et al. and the experimental work of the four-component fluid system, $(NH_4)_2SO_4$-water-ethanol-benzene.

1. Introduction

The name tricritical point was proposed for a certain type of phase transition by Griffiths [1]. In phase transitions, it is found experimentally that a first order phase transition turns into a lambda transition at a particular temperature, which is seen to be the terminus of three critical lines. Alternatively, the tricritical point is also the terminus of a line of triple points at which all three coexisting phases identical simultaneously.

The tricritical points have been found in metamagnets, antiferromagnetic systems, $He^3 - He^4$ mixtures, antiferroelectric systems, and in multicomponent fluid mixtures [2-9]. When the Hamiltonians possess special symmetries associated tricritical points are usually refered to as symmetrical tricritical points. On the other hand, when the Hamiltonian do not have any symmetries, then the unsymmetry tricritical points found.

Higher order critical points in multicomponent fluids pointed out by Kohnstamm in 1926 [10] were received relatively little attention until the recent discovery by Widom [11-15]. The absence of appropriate symmetries in fluids system necessitate a rather extensive theoretical frame work. The classical models which are stated based on the expansion of a free energy in powers of an order parameter, are stated in terms of an appropriate set of scaling fields. It is complicated to relate these scaling fields to physical thermodynamic variables such as temperature, pressure, and chemical potentials. The choice of field parameters has been examined by comparing the classical model with the result of various optical experiments by Kim et al. [16].

Recently a test of mean-field behavior through power-law analysis in asymmetric system has been reported by Kim et al.. Gollub et al. tested mean-field predictions from the Rayleigh linewidth dependence on temperature [17], and Wu tested these predictions for the temperature dependence of the scattering intensity. [18,19]

An outline of this paper is as follows. Section 2 is devoted to the introduction to the critical point developed by Griffiths. The experimental results for multicomponent fluid system are reported in Sec. 3. The experimental results on tricritical point were performed in a four component mixture, ammonium sulfate-ethanol-water-benzene. This paper is intended as an introduction to the study of the multicritical points in many systems, and the theory of the phase transition is reviewed at an introductory level.

2. The Classical Model

In this section we present the basic formulas for a Landau theory employing a single order parameter and the extended treatments developed by Griffiths et al. [6,7]. Schulman and his collaborators have used the theory of catastrophes for classifying critical points. [20] Okada and Suzuki, also discussed the multicritical points by the catastrophe theory. [21]

Catastrophe theory provides a phenomenological model of phase transitions. Schulman et al. claimed that the catastrophe theory is superior to the Landau model in allowing for non classical exponents. Following Griffiths and Wheeler [7], we shall call intensive variables, such as pressure, temperature chemical potential, the *field* and extensive variables the

denities.

Griffiths suggested that there are at least two conceptual advantages in using fields alone as independent variables when one wishes to obtain a qualitative understanding of some phase transition phenomena. The first is that the phase diagrams are simpler to draw in a field space than they are in a density space, or a space of mixed densities and fields. The second is that a very useful tool is to focus attention on a section a hyperplane of lower dimensionality.

The Landau thermodynamic theory of ordinary critical points is of value because of its great simplicity. In a first approximation, we assume that an appropriate free energy Ψ can be expanded in a power series in

$$\Psi = a_1 \varphi + a_2 \varphi^2 + a_3 \varphi^3 + a_4 \varphi^4 + \varphi^6 \quad (1)$$

where φ is a one-dimensional order parameter or a density. The a_5 term has been omitted because, were it present, it could be eliminated by replacing φ. The coefficient a_6 is set equal to unity because it must be positive (for thermodynamic stability). Ψ is a global minimum for $-\infty < \varphi < \infty$. As has no influence on the thermodynamic state, the minimum value of Ψ is set equal to zero. The coefficients a_i are functions of the physical fields which appear in the Hamiltonian of the system. One can expand the a_i in power series in the physical fields. The fact that the a_i are related to the physical fields by a linear transformation implies that the topology of the phase diagram should be the same in the a_i space and the space of the physical fields. [8]

The phase diagram should be obtained by studying in the minima of the free energy. To study the minima, it is convenient to rewrite the free energy in the form [8]

$$\Psi = \prod_{j=1}^{3} \{ (\varphi - b_j)^2 + d_j \} \quad (2)$$

where the b's and d's are real, the d's are nonnegative, and at least one of the d's is zero [8]. The phase diagram corresponding this free energy in the (b_j, d_j) space is summarized in Table I.

By varying one or more fields it is possible to make two coexisting phases move closer together until they coalesce to from a critical point, which is denoted by B. Likewise we denote three coexisting phases by AAA, tricritical point by C. These nota-

Table I. Critical and coexistence surfaces

No.	Type of surface	Equations	f	Manifold
1	Tricritical points	$b_1 = b_2 = b_3$ $d_1 = d_2 = d_3 = 0$	0	C
2	Critical end points	$b_1 = b_2$ $d_1 = d_2 = d_3 = 0$	1	B A
3	Critical points	$b_1 = b_2$ $d_1 = d_2 = 0$	2	B
4	Triple points	$d_1 = d_2 = d_3 = 0$	2	A^3
5	Two coexisting phases	$d_1 = d_2 = 0$	3	A^2

tions are listed also in Table I. Figure 1 shows the potential schematically. Figure 2 is the configurations in the b, d plane. [9]
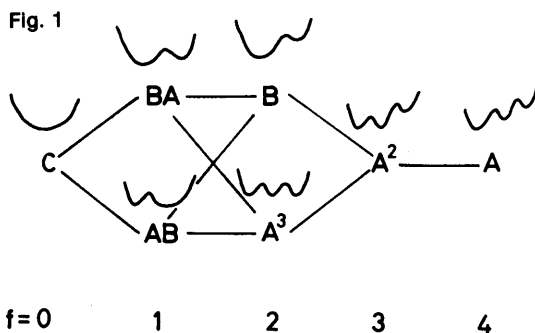

Fig. 1

f = 0   1   2   3   4

Fig. 1 The forms of the free energy and characteristic graph for a tricritical point C. f is the dimension of the manifolds.
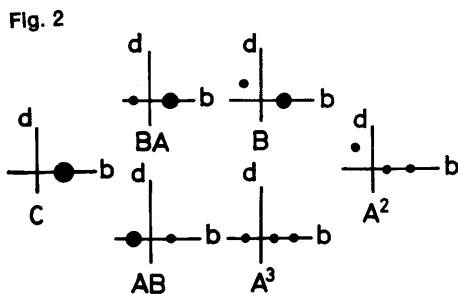

Fig. 2

Fig. 2 Configurations in the b, d plane.

The expressions for a_1, a_2, a_3, and a_4, simplified with the relation

$$b_1 + b_2 + b_3 = 0 \quad (3)$$

are given in Appendix. Eq. (3) are given by the requirement $a_5 = 0$.

Let us consider the singular points. The results are given in Appendix.
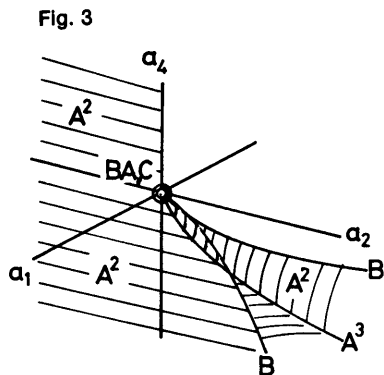
The manifolds are depicted in Fig.3 schematicaly.

Fig. 3

Fig. 3 Schematic diagram corresponding to the free energy (1) in the case of $a_3 = 0$.
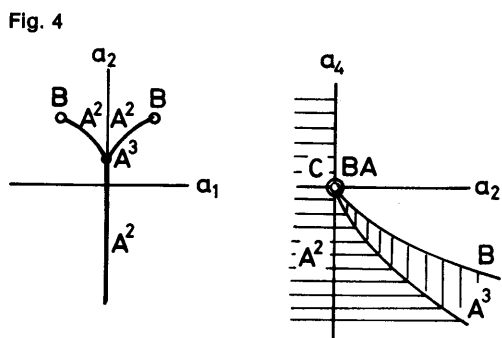
Fig. 4

Fig. 4 Phase diagrams in the (a_1, a_2) and (a_2, a_4) planes.

For the case of $a_3 = 0$, the (a_1, a_2) phase diagram are shown in Fig.4, which correspond the e-t phase diagram in ferroelectric phase transition.

The Gibbs phase rule states that the coexistence of m phase in a system composed of c components has [9]

$$f = c + 2 - m \qquad (4)$$

degree 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

$$\kappa = m - 1. \qquad (5)$$

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.
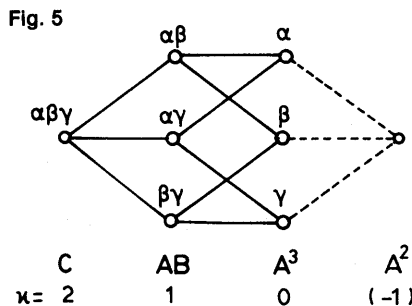
Fig. 5

Fig. 5 Characteristic graph for three phases coexistence. Phases are labeld α, β and γ.

In the three phase region, the Landau theory predicts that the susceptibilities in the different phases are related by sum rules. [5] The susceptibility χ in phase 1 is defined by

$$\chi_1^{-1} = (d^2\Psi/d\varphi^2) = 2(b_1 - b_2)^2 (b_1 - b_3)^2 \qquad (6)$$

and similarly χ_2^{-1} and χ_3^{-1}
The first sum rule

$$\chi_1^{1/2} + \chi_2^{1/2} - \chi_3^{1/2} = 0 \qquad (7)$$

is derived from (6).
The second sum rule

$$\chi_1^{-1/2} + \chi_2^{1/2} - \chi_3^{1/2} = -3a_4/\sqrt{2} \qquad (8)$$

comes from $b_1 + b_2 + b_3 = 0 = a_5$, where $a_4 = 2(b_1 b_2 + b_2 b_3 + b_3 b_1)$. Other results, such as

$$\chi_1^{-1} + \chi_2^{-1} + \chi_3^{-1} = \frac{9}{2} a_4^2 \qquad (9)$$

can be obtained. [5]

The sum rules are of practical interest because (7) should hold throughout the three-phase region, and the right-hand side of (8) depends only temperature if we make the identification

$$a_4 \sim (T/T_{TCP} - 1) \qquad (10)$$

Lang and Widom [22] have carried out careful measurements of the compositions of a number of cases of three coexisting phases in the mixture water-ethanol-benzene-ammonium sulfate. Kaufman et al. [23] show how such information can be combine with (1) and the relationship between a_j, φ and quantities observed experimentally. The intensity of light I is proportional to $\langle (\delta \epsilon)^2 \rangle$, where ϵ is the dielectric

constant. Therefore, I should be proportional to χ times a term which tends to a constant at the tricritical point. Kaufman et al. showed the classical model is in good agreement with results of light scattering measurements in the three phase region. [23]

3. The Mixture Ammonium Sulfate-Water-Ethanol-Benzene

The experimantal discovery of tricritical points has been ascribed to Efremova by her colleagues.[13] The first published report of a tricritical point in a three component system is that by Krichevskii et al. on the mixture acetic acid-water-butane, while an even earlier paper by Radyshevskaya, Nikurasina, and Mertslin [24,25] reports the discovery of a tricritical point in the four-component system $(NH_4)_2SO_4$-water-ethanol-benzene.

In the three component systems the tricritical points may be described as of the liquid-liquid-gas type. In four component methanol-ethanol-water-carbon dioxide system, there is a one-parameter family of such liquid-liquid-gas tricritical points. But the tricritical points in the four-component systems $(NH_4)_2SO_4$-water-ethanol-benzene may be described as of the liquid-liquid-liquid type, since in these cases the three phases that become identical are three ordinary liquid solutions. In such three liquid phase system, it is convenient to look upon the pressure as the parameter that varies along the locus of tricritical points.

Three phases α, β and γ in equilibrium are pictured in Fig.6. The condition in which the phases α

Fig. 6

$$\alpha,\beta,\gamma \qquad (\alpha\beta)\gamma \qquad \alpha(\beta\gamma) \qquad \alpha\beta\gamma$$
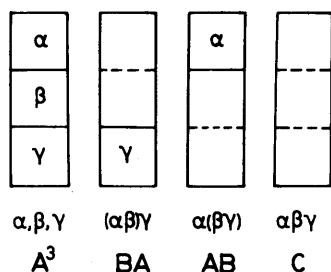$$A^3 \qquad\quad BA \qquad\quad AB \qquad\quad C$$

Fig. 6 Schematic illustration of critical points and a tricritical points. Three liquid phases α, β and γ are presented in a closed tube. Soild lines indicate meniscuses and broken lines meniscuses which have just disapeared at a critical point.

and β becomes identical while they are still in equilibrium with the distinct phase γ is a critical end point, and may be symbolized by $(\alpha\beta)\gamma$. [BA] The schematic projection of that locus onto the pressure temperature plane is shown in Fig.7. The second
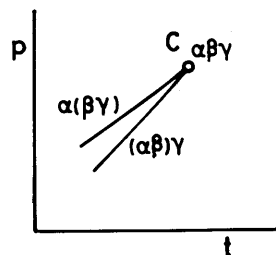
Fig. 7

Fig. 7 Projection onto the pressure-temperature plane of two loci of critical end points. The tricritical point, marked with a circle, is at the confluence of two loci.

curve marked $\alpha(\beta\gamma)$, is the projection of the locus of critical end points at which phases β and γ have become identical. The tricritical point [C] occurs at the confluence of these two loci, where the three phases α, β and γ become identical.

Let the phases α, β and γ in Fig.6 now represent the three liquid phases that can be in equilibrium in the $(NH_4)_2SO_4$-water-ethanol-benzene system. The top layer α is always the benzene rich layer, which is the least dense, while bottom layer γ is always the salt rich layer, which is the most dense. The $\alpha\beta$ phase equilibrium is essentially the same as that with occurs in the three component system water-ethanol-benzene, were there is no $(NH_4)_2SO_4$, while the $\beta\gamma$ phase equilibrium is essentially the same as that which occurs in the three component system $(NH_4)_2SO_4$-water-ethanol, where there is no benzene.

Widom prepared six mixtures at room temperature [11], all containing $(NH_4)_2SO_4$:water:ethanol in the ratios 1:4.2:4.2 by mass, but with varying amounts of benzene. The $\beta\gamma$ meniscus, associated with the salting-out, is razor sharp, while $\alpha\beta$ meniscus has a thick and oily appearance. The $\alpha\gamma$ meniscus is in that respect intermediate.

The workers who discovered the tricritical point in the $(NH_4)_2SO_4$-water-ethanol-benzene system [23] estimated it occur at a temperature close to 49°C and at a composition in which the mass fraction of

$(NH_4)_2SO_4$ is 0.004 ± 0.01 while the ratio of the water and ethanol masses is 1.0 ± 0.2. This still leaves the benzene content unspecified. Widom prepared a mixture with the mass fractions $(NH_4)_2SO_4 = 0.04$, water $= 0.28$, ethanol $= 0.33$, and benzene $= 0.35$. At room temperature all three liquid phases were present, with the γ phase occupying about 1/5 the total volume, but, as the temperature was raised the $\beta\ \gamma$ meniscus rose slowly, the $\alpha\ \beta$ meniscus fall rapidly, and at 42°C they joined. The heights of the meniscuses separating various phases inside a sealed tube were measured as a function of temperature in several different experiments. [5,18,19] Kaufman et al. compared the experimental results with their model, using the fraction of volume.

We reexamined the critical phenomena in liquid system. Our preliminary results are only short reports, because our set up of experiments are not complete. We add I_2 in $(NH_4)_2SO_4$-water-ethanol-benzene fluid mixture, then we were easily determine the temperature dependences of meniscus height. Our system is not completely sealed out, then the tricritical point were not observed. Figure 8 shows the meniscus heights as a function of the temperature. The critical point BA were observed at about 73°C.
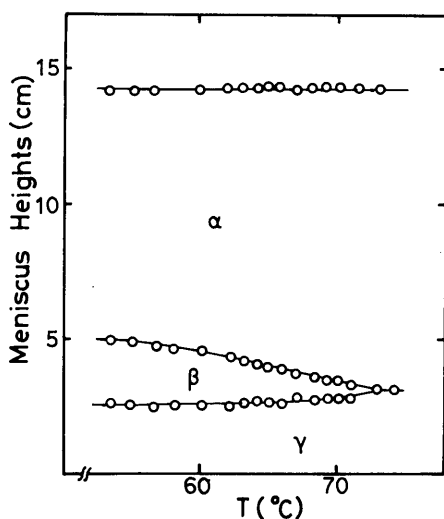
Fig. 8

Fig. 8 Meniscus height as a function of the temperature.

4. Summary

We have discussed the model based on the Landau theory of expanding a free energy in terms of order parameter φ. We showed the singular manifolds, such as C, B, BA, A^3 and A^2, and figured out the topological space in the case of $a_3 = 0$. We discussed these singular points by comparing with the experimental works of fluid mixture, ammonium sulfate-water-ethanol-benzene. Because of the absence of appropriate symmetries, the theoretical and experimental works of fluid mixture are very important. It would be very useful to have an appropriate non-classical equations of state near the singular points.

Appendix

$$\Psi = [(\varphi - b_1)^2 + d_1][(\varphi - b_2)^2 + d_2][(\varphi - b_3)^2 + d_3]$$
$$= [\varphi^2 - 2b_1\varphi + c_1][\varphi^2 - 2b_2\varphi + c_2][\varphi^2 - 2b_3\varphi + c_3]$$
$$= \varphi^6 + a_5\varphi^5 + a_4\varphi^4 + a_3\varphi^3 + a_2\varphi^2 + a_1\varphi + a_0$$

where $c_i^2 = b_i^2 + d_i$.

$$a_1 = -2(b_3c_1^2c_2^2 + b_1c_2^2c_3^2 + b_2c_1^2c_3^2)$$
$$a_2 = c_1^2c_2^2 + c_2^2c_3^2 + c_3^2c_1^2 + 4b_1b_2c_3^2 + 4b_2b_3c_1^2 + 4b_3b_1c_2^2$$
$$a_3 = -2[(b_1 + b_2)c_3^2 + (b_1 + b_3)c_2^2 + (b_2 + b_3)c_1^2 + 4b_1b_2b_3]$$
$$a_4 = c_1^2 + c_2^2 + c_3^2 + 4b_1b_2 + 4b_2b_3 + 4b_3b_1$$

[I] Tricritical points   C : f = 0
$a_1 = a_2 = a_3 = a_4 = 0$.

[II] Critical end points   BA : f = 1
$a_1 = -12b_1^5$
$a_2 = 9b_1^4$
$a_3 = 4b_1^3$
$a_4 = -6b_1^2$

[III] Critical points   B : f = 2
$a_1 = -4b_1^3(3b_1^2 + d_3)$
$a_2 = 9b_1^4 + 6b_1^2d_3$
$a_3 = 4b_1(b_1^2 - d_3)$
$a_4 = -6b_1^2 + d_3$

[IV] Triple points   AAA : f = 2
$a_1 = (a_3/2)a_4$
$a_2 = a_4^2/4$
$a_3 = 2b_1b_2(b_1 + b_2)$

$a_4 = -2(b_1{}^2 + b_2{}^2 + b_1b_2)$

[Ⅴ] Two coexisting phases   AA : f = 3

$a_1 = -2b_1b_2(b_1 + b_2)(b_1{}^2 + b_2{}^2 + b_1b_2 + d_3)$

$a_2 = (b_1 + b_2)^2(b_1{}^2 + b_2{}^2) + b_1{}^2b_2{}^2 + d_3(b_1{}^2 + b_2{}^2 + 4b_1b_2)$

$a_3 = 2(b_1 + b_2)(b_1b_2 - d_3)$

$a_4 = -2(b_1{}^2 + b_2{}^2 + b_1b_2) + d_3$

References

1] R.B.Griffiths:Phys. Rev. Lett. **24** (1970) 715.

2] I.Suzuki and Y.Ishibashi:J.Phys. Soc. Jpn. **52** (1983) 187.

3] I.Suzuki and Y.Ishibashi:J.Phys. Soc. Jpn. **52** (1983) 2088.

4] Y.Ishibashi and I.Suzuki:J.Phys. Soc. Jpn. **52** (1983) 2443.

5] M.Kaufman and R.B.Griffiths:J.Chem. Phys. **76** (1982) 1508.

6] R.B.Griffiths:J.Chem. Phys. **60** (1974) 195.

7] R.B.Griffiths and J.C.Wheeler:Phys. Rev. A**2** (1970) 1047.

8] S. Krinsky and D. Mukamel:Phys. Rev. B**11** (1975) 399.

9] R.B.Griffiths:Phys. Rev. B**12** (1975) 345.

10] Ph.Kohnstamm, in *Handbuch der Physik*, edited by H.Geiger and K.Scheel (Springer, Berlin, 1926) vol.10 p223.

11] B.Widom:J.Phys. Chem. **77** (1973) 2196.

12] R.B.Griffiths and B.Widom:Phys. Rev. A**8** (1973) 2173.

13] G.D.Efremova and A.V.Shvarts:Russ. J.Phys. Chem. **40** (1966) 486, **43** (1969) 968, **46** (1972) 237.

14] A.V.Shvarts and G.D.Efremova:Russ. J.Phys. Chem. **44** (1970) 614.

15] R.B.Griffiths:J.Chem. Phys. **71** (1979) 15.

16] M.W.Kim and W.I.Goldburg:J.Chem. Phys. **71** (1979) 15.

17] J.P.Gollub, A.A.Koenig, and J.S.Huang:J.Chem. Phys. **65** (1976) 639.

18] E.S.Wu:Phys. Rev. A**18** (1978) 1641.

19] M.W.Kim, W.I.Goldburg, P.Esfandiari, J.M.H.Levelt Sengers and E.S.Wu:Phys. Rev. Lett. **44** (1980) 80.

20] L.S.Sculman:Phys. Rev. B**7** (1973) 1960.

21] K.Okada and I.Suzuki:J.Phys. Soc. Jpn. **51** (1982) 3250.

22] J.C.Lang, Jr., and B.Widom:Physica **81**A (1975) 190.

23] M.Kaufman, K.K.Bardham, and R.B.Griffiths: Phys. Rev. Lett. **44** (1980) 77.

24] R.V.Mertslin and K.I.Mochalov:Zh. Obschch. Khim. **29** (1959) 3172.

25] G.S.Radyshevskaya, N.I.Nikurashina, and R.V. Mertslin:J.Cen. Chem. USSR. **32** (1962) 673.