

## The tricritical point — a qualitative overview

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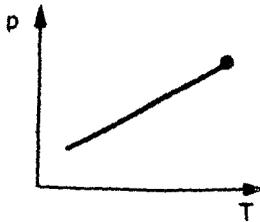
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**Abstract.** The concept of tricritical points is introduced by way of examples of ordinary liquid mixtures and mixtures of normal  $\text{He}^3$  and superfluid  $\text{He}^4$ . A prototype Ising spin model is used for a qualitative discussion of the mechanisms behind the occurrence of tricritical phenomena. Mention is also made of the other theoretical developments.

**Keywords.** Phase transition; critical phenomena; tricritical points.

### 1. Introduction

The aim of this paper is to provide a brief introduction to tricritical phenomena. The occurrence of tricritical points can be most easily understood in terms of critical phenomena in liquid mixtures (Griffiths 1974). To begin with, we consider the phase diagram for the simplest system, a pure fluid near a liquid-vapour critical point. In a space of the "field" variables  $p$  and  $T$  (variables that are the same in the two co-existing phases), the co-existence curve is a single line which terminates at a critical point (indicated by a dot in figure 1), where the properties of the two coexisting phases become identical to one another. What happens next if we add one more component, *viz.*, we consider a binary mixture? The coexistence curve in the space  $p, T$  and say  $\mu_2$ , the chemical potential of the second component, now becomes a



**Figure 1.** Phase diagram for a single component fluid near the liquid-vapour critical point in the  $p, T$  plane.

two dimensional surface (hatched region) terminating in a line (solid one) of critical points (Figure 2a). Several binary mixtures, however, exhibit both liquid-vapour and liquid-liquid critical lines. Figure 2b shows schematically the phase diagram in which there is one coexistence surface for liquid-vapour phase separation and one for liquid-liquid phase separation. The latter terminates where it meets the former along a line of triple points  $BC$ . The point  $C$  is a "critical end point" at which two coexisting phases have become identical in the presence of a third phase.

Ordinarily, in a binary mixture, the Gibbs phase rule precludes the intersection of the two critical lines  $AA'$  and  $CD$  (see figure 2b). However, imagine that one more component is added so that one has a ternary mixture. The situation may be visualized by imagining a closed tube (figure 3) in which three distinct fluid phases lie on top of each other. At a critical end point one of the two meniscuses disappears (indicated in figure 3b and 3c by a row of vertical lines) while the remaining two phases stay distinct. If both meniscuses vanish simultaneously, three phases become identical, and one has a tricritical point. If we were to construct the phase diagram for the ternary system, we would have to employ four field variables (say,  $p$ ,  $T$  and two chemical potentials). However, if we hold one thermodynamic field, say  $\mu_3$  fixed, the resulting three-dimensional section looks qualitatively similar to that

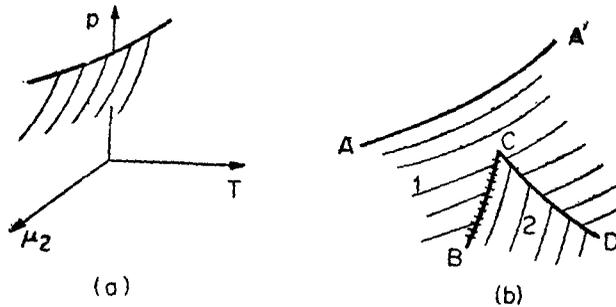


Figure 2a. Phase diagram for a binary liquid mixture near a line of critical points.

Figure 2b. Phase diagram (schematic) showing, in an appropriate space of field variables, portions of the coexistence surfaces for a binary mixture with a liquid-vapour critical line  $AA'$  and a liquid-liquid critical line  $CD$ , shown as heavy lines. The two coexistence surfaces 1 and 2 (indicated by lighter lines) meet along the line of triple points  $BC$ .

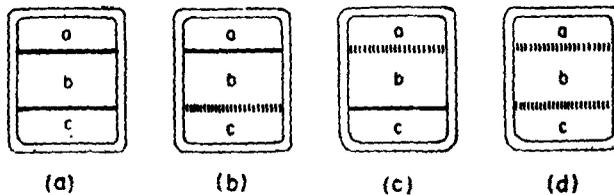
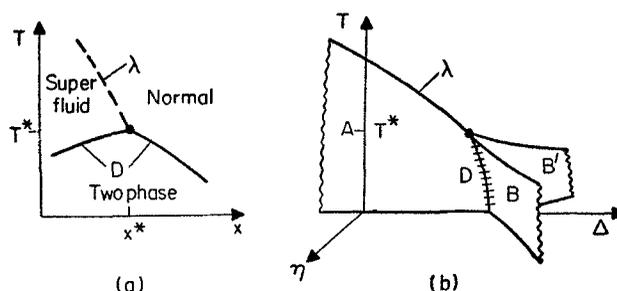


Figure 3. Three liquid phases  $a$ ,  $b$  and  $c$  are present in a closed tube (a) separated by two meniscuses. At a critical end point two of the phases become identical in the presence of a third phase (b) or (c). In (d) both meniscuses vanish simultaneously and one has a tricritical point.

shown in figure 2b. Now as  $\mu_3$  is allowed to vary continuously, the phase diagram in figure 2b is expected to deform continuously, and eventually, the two lines of critical points might intersect. To put it somewhat differently, one could reach a situation in which the triple line marches all the way up to meet the line of critical points  $AA'$ . The confluence point will be a tricritical point at which the three phases coexisting along the triple line become simultaneously identical. Thus a tricritical point in a ternary mixture is an isolated point, and four variables *e.g.*,  $p$ ,  $T$ , and the two independent composition ratios (say,  $x_1$  and  $x_2$ ) in the mixture must be precisely correct in order to obtain a tricritical point. Extending this argument, in a quaternary (four-component) mixture, with one more degree of freedom, one would obtain a line of tricritical points, etc.

## 2. Other systems

The preceding discussion might convey the impression that one needs at least three components to obtain a tricritical point in liquid mixtures. However, a tricritical point can occur even in a binary system if the various phases are related by symmetry. Consider for example a mixture of normal  $\text{He}^3$  and superfluid  $\text{He}^4$  (the latter, by itself, can exist in two different phases related by a symmetry operation). Under saturated vapour pressure, it is observed that the  $\lambda$  transition temperature decreases with increasing mole fraction  $x$  of  $\text{He}^3$ , and below a temperature  $T^* = 0.87\text{K}$  corresponding to  $x = 0.67$ , a first order phase separation takes place (figure 4a). Figure 4b shows the phase diagram at constant pressure in terms of  $T$ ,  $\Delta = \mu_3 - \mu_4$  (the field conjugate to  $x$ ) and a fictitious "field"  $\eta$  conjugate to the superfluid order parameter  $\Psi$ . One has a first order coexistence surface  $A$  in the  $\eta = 0$  plane which extends to  $\Delta = -\infty$  (pure  $\text{He}^4$ ). On  $A$ ,  $\Psi$  assumes nonzero values with opposite signs depending on whether  $\eta \rightarrow 0$  from positive or negative directions. As  $T$  increases, the surface  $A$  terminates in a line of critical points, the  $\lambda$  line, and for  $T < T^*$ , terminates in the two-fluid coexistence curve  $D$ . Looking at figure 4 one notes that  $A$  is connected along the line  $D$  to two first order (coexistence) surfaces  $B$  and  $B'$ , extending symmetrically into the regions  $\eta > 0$  and  $\eta < 0$ , respectively. The surfaces  $B$  and  $B'$  themselves terminate with increasing temperature in lines (solid ones) of critical points. These two critical lines and the  $\lambda$  line join together at the tricritical point.



**Figure 4a.** Phase diagram (schematic) for  $\text{He}^3$ - $\text{He}^4$  mixtures. The two fluid coexistence curve is labeled  $D$ , the dashed curve is the line of lambda transitions and the dot indicates the tricritical point. **(b)** Phase diagram for  $\text{He}^3$ - $\text{He}^4$  mixtures in the field space. Only the  $\eta = 0$  plane is experimentally accessible.

point. Therefore, the tricritical point may be regarded either as the termination of a line ( $D$ ) of triple points (the point of view adopted earlier in the case of ternary liquid mixtures), or equivalently, as the confluence of three lines of critical points. In fact, it is the latter feature which prompted Griffiths (1970) to name the special point a tricritical point. In addition to He<sup>3</sup>-He<sup>4</sup> mixtures, tricritical points have been observed also in antiferromagnets in an external magnetic field (see, for instance, Landau *et al* 1971) and structural phase transitions (see, for example, Yelon 1974).

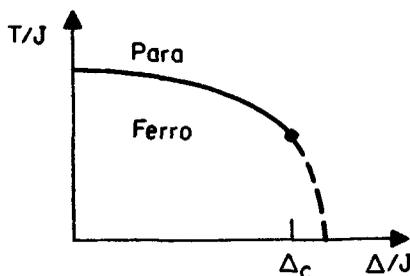
### 3. Model discussion

The present analysis is based on what is now called the Blume-Capel model (Blume 1966; Capel 1966; also see Blume 1974). Imagine a Hamiltonian which describes an Ising-type interaction between nearest neighbour spin-1 ions in a lattice which are subject also to a crystal field  $\Delta$  :

$$\mathcal{H} = -J \sum_{\langle ij \rangle} S_i S_j + \Delta \sum_i S_i^2, \quad \Delta > 0. \tag{1}$$

Here  $S_i = \pm 1$  or 0. For small enough  $\Delta$ , the single ion energy levels  $S_i = \pm 1$  lie not much higher than the  $S_i = 0$  singlet and so the exchange interaction remains operative. Under this condition, mean field calculations suggest that the paramagnetic-ferromagnetic transition is of second order. As  $\Delta$  is increased beyond a critical value  $\Delta_c$ , the transition changes into a first order one and the cross-over occurs at a tricritical point (figure 5). As  $\Delta$  is increased still further, the transition temperature decreases and goes to zero. This is so because, for a large value of  $\Delta$ , the  $S_i = \pm 1$  levels become inaccessible and hence the exchange interaction becomes inoperative. The meaning of the various phases becomes clearer if one considers an applied magnetic field  $H$  in addition to the crystal field and exchange terms in (1). The phase diagram then becomes qualitatively similar to the one seen in He<sup>3</sup>-He<sup>4</sup> mixtures (figure 4b) in which  $\eta$  now plays the role of  $H$ .

The following feature about the various terms in the Hamiltonian in (1) is worth noting in our understanding of tricritical behaviour. First, one has the usual magnetic order  $M = \langle S_i \rangle$  which characterizes the ferromagnetic to paramagnetic transition. In addition, one has, for this spin-1 system, a quadrupolar order para-



**Figure 5.** Phase diagram in the  $T$ - $\Delta$  plane. For  $\Delta < \Delta_c$ , one has a second order transition from the para-to-ferro-magnetic phases. For  $\Delta > \Delta_c$ , the transition changes over into first order (dashed line).

meter  $Q = \langle S_i^2 \rangle$ . Note that the field  $\Delta$  which is conjugate to  $Q$  plays the same role as  $H$  does with respect to  $M$ . Further, the order parameters  $M$  and  $Q$  are not totally independent of one another. For example, it is not possible to have a stable state in which  $M=1$  and  $Q=0$ , since  $M=1$  requires that all the spins have  $S_i=1$  which in turn leads to  $Q=1$ . The two-order parameters are therefore *kinematically coupled* in the sense that even in the absence of interactions, there are constraints on the values which can be taken on by the two together. It is the competition between two kinematically coupled order parameters which is eventually responsible for the occurrence of first order phase transitions, tricritical points, etc. The exchange term in (1) gives a lower energy for  $M=1$ , while the crystal field term favours  $Q=0$ . These two values are incompatible, however. The increase in  $\Delta$  ultimately makes it more favourable energetically to have  $Q=0$  (and hence  $M=0$ ) than  $M=1$ .

#### 4. Other theoretical approaches

In addition to the usual molecular field theory analysis mentioned above, tricritical points in ternary and quaternary fluid mixtures have been investigated in detail within the Landau model (Griffiths 1974). Very similar discussions, although couched in the language of "catastrophes", have been presented by Schulman (1973). From the latter point of view, the occurrence of a tricritical point may be viewed as a butterfly catastrophe (see, for instance, Majumdar 1980). Scaling theories have been proposed also (see, for example, Riedel 1972) and the usual scaling laws are expected to hold at the tricritical point, with allowance for the changed exponents. The mean field values of the tricritical exponents are listed in table 1 along with the corresponding values of ordinary critical exponents, for the sake of comparison. One may see, for instance, that the energy scaling which yields  $\alpha + 2\beta + \gamma = 2$  holds for tricritical phenomena also.

A major part of the activities in recent years concerning tricritical points is centred around renormalization group calculations. The most important outcome of such studies is the result that the mean field values of the exponents are correct, with logarithmic corrections, for tricritical points in *three* dimensions (Riedel and Wegner 1972).

Table 1. Meanfield exponents for critical and tricritical points.

		Ordinary critical point	Tricritical point
$\alpha$	..	0	1/2
$\beta$	..	1/2	1/4
$\gamma$	..	1	1
$\delta$	..	3	5

## 5. Conclusions

We would like to conclude this presentation by returning to the example of ternary liquid mixtures that we discussed in the beginning. We have investigated recently (Furman *et al* 1977) the global features of the phase diagram of a general three component Ising model on a lattice whose Hamiltonian may be expressed as

$$\begin{aligned} \mathcal{H} = & -q^{-1} J \sum_{ij} S_i S_j - q^{-1} K \sum_{ij} S_i^2 S_j^2 - q^{-1} C \sum_{ij} (S_i^2 S_j + S_i S_j^2) \\ & - H \sum_i S_i + \Delta \sum_i S_i^2. \end{aligned} \quad (2)$$

Here each spin  $S_i = 0$ , or  $\pm 1$ , and  $q$  is the coordination number of the lattice. With suitable interpretation, this model may be viewed as (i) a spin-1 Ising magnet for which the various terms in (2) represent respectively dipolar exchange, quadrupolar exchange, mixed dipolar-quadrupolar exchange, coupling with an external field  $H$  and crystal field interaction. (Normally, for a magnet in zero magnetic field,  $C$  vanishes due to time reversal invariance.); (ii) a three-component lattice gas in which the volume of the system is imagined to be divided into cells whose centres form a regular lattice. Each cell contains one and only one of three types of molecules; (iii) a regular solution model of a three-component mixture, in the molecular field approximation. It is this last feature that we want to address to here.

Solving for the grand partition function for the system described by (2) in the molecular field approximation, one may derive for the Gibbs potential

$$G = \bar{a}yz + \bar{b}xz + \bar{c}xy + x \ln x + y \ln y + z \ln z, \quad (3)$$

where the variables  $x$ ,  $y$  and  $z (= 1 - x - y)$  are related to the dipolar order parameter  $M$  and quadrupolar order parameter  $Q$  introduced in § 3:

$$x = \frac{1}{2}(Q + M), \quad y = \frac{1}{2}(Q - M), \quad Z = 1 - Q. \quad (4)$$

The "energy" parameters  $\bar{a}$ ,  $\bar{b}$  and  $\bar{c}$  are given in terms of the Boltzmann constant  $k$ , the temperature  $T$  and the parameters appearing in the Hamiltonian in (2):

$$\bar{a} = \frac{1}{2kT} (J + K - 2C), \quad \bar{b} = \frac{1}{2kT} (J + K + 2C), \quad \bar{c} = \frac{2J}{kT}. \quad (5)$$

It is evident that  $x$ ,  $y$  and  $z$  in (3) can be interpreted as the molefractions of a three-component system ( $x = N_x/N$ , etc.,  $N = N_x + N_y + N_z$ ) whose free energy is given by (3) in a "regular solution" model. Note that the model has certain symmetries. For instance, if  $\bar{a} = \bar{b} = \bar{c}$ ,  $G$  is invariant under the permutation of  $x$ ,  $y$  and  $z$ . Consequently, one finds, in addition to tricritical points, lines of tricritical points, four phase coexistence region and three fourth order points at which four coexisting phases become simultaneously identical.

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