A QUALITATIVE PICTURE OF THE TRICRITICAL POINT*

M. Blume

Brookhaven National Laboratory

Upton, New York 11973 U.S.A.; and

State University of New York at Stony Brook

Stony Brook, New York 11790 U.S.A.

INTRODUCTION

The liquid-gas phase transition, when viewed in the pressure-temperature plane, consists of a line of first-order transitions which end in a critical point, beyond which a continuous transition between the two phases is possible. Such a phase diagram is not possible for all types of transitions, however, as was indicated by Landau.¹ In particular, if the two phases differ from one another by symmetry, as in the paramagnetic-ferromagnetic transition in the absence of an external field, or in most structural phase changes, it is always possible in principle to say in which of the two phases the system is. A line of first-order transitions could not, for these systems, end in a critical point, but it is possible for the line to change into a line of second-order. The critical phenomena at the point where the changeover from first- to second-order occurs are quantitatively different from those at an ordinary critical point or second-order transition. Theoretical examples of such changeovers were found in a number of models of magnetic systems, and some of the properties of these points were worked out.²⁻⁴ In addition, experimental examples of this changeover, such as the behavior of the Ising antiferromagnet Dysprosium Aluminum Garnet in an external magnetic field⁵ and phase separation in mixtures⁶ of He^3 and He^4 were found.

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A new period of activity, both experimental and theoretical, in the study of critical phenomena in the vicinity of this "change-over" point, and, indeed, a new name for this point, began with the observation by Griffiths⁷ that, when viewed in a space of suitable thermodynamic variables, this point was the intersection of three lines of critical points. Accordingly, Griffiths proposed the name "tricritical" point, a name which was rapidly adopted. Since his paper there have been many studies of the properties of the tricritical point. The purpose of this lecture is to provide an introductory view of tricritical phenomena and an indication of some of the theoretical and experimental work in progress.

II. QUALITATIVE DISCUSSION OF A MODEL

To illustrate the concepts involved in the description of the tricritical point we will give a qualitative treatment of a model which displays a tricritical point. We consider a lattice with spin-one ions at each site. These ions interact with a nearest-neighbor Ising-type interaction. In addition we allow a crystal-field interaction and an interaction with an external magnetic field. The full Hamiltonian is

$$\mathcal{H} = -J \sum_{\langle ij \rangle} S_i S_j + \Delta \sum_i S_i^2 - H \sum_i S_i \quad (1)$$

Here $S_i = \pm 1$ or 0. The term proportional to Δ gives single spin energy levels, for $\Delta > 0$, with an $S_i = 0$ singlet level lowest and $S_i = \pm 1$ degenerate and at an energy Δ above the singlet. Systems of this type have been studied, with application to magnetism in mind, in the molecular field approximation,^{3,4} and, more recently, by the techniques of series expansion analysis^{8,9} and Monte Carlo calculation.¹⁰ The main conclusion of all of these analyses has been that the paramagnetic-ferromagnetic phase transition is, for small enough Δ , a second-order transition. As Δ is increased a critical value Δ_c is found at which the transition becomes first-order. As Δ is increased still further, the discontinuity in the order parameter at the transition increases and the transition temperature decreases. Finally, Δ becomes sufficiently large so that the $S_i = 0$ level lies sufficiently low that the exchange interaction, which acts only on the $S_i = \pm 1$ levels, is ineffective, and the system does not order. There are of course quantitative differences between the mean field results and the Monte Carlo and series expansion calculations, but on the whole the latter have shown that the mean-field results are qualitatively correct, and we will therefore rely on the latter for the qualitative discussion here.

The results of the mean-field calculation of the phase-diagram

in the T - Δ plane for external magnetic field $H = 0$ are shown in figure 1.

Figure 1. Phase diagram in the T - Δ plane for the mean field solution of Eq. (1). The solid lines represent second-order transitions; dashed lines represent those of first-order. The tricritical point is denoted by A (from Ref. 11).

Here the solid line represents the second-order transition between the ferromagnetic and paramagnetic phases (below and above the line, respectively). At the point A, the tricritical point, the transition changes from second- to first-order, and for $\Delta/J = 0.5$, the transition disappears altogether, and the system is non-magnetic even at $T = 0$. To understand the nature of the tricritical point more completely we must consider the effects of an external field on the system. Before doing this, a few points about the Hamiltonian should be noted. There are two order parameters which are represented by terms in the Hamiltonian to be considered in this problem. These are, first, the ordinary magnetic order $M = \langle S_z \rangle$. The vanishing or nonvanishing of M , in the absence of an external field H , characterizes the system as paramagnetic or ferromagnetic, and the transition lines in figure 1 represent the points at which M changes from zero to a non-zero value. The change is continuous at the solid second-order line, and discontinuous at the dashed first-order line. Two terms in the Hamiltonian (1) affect this order parameter directly. These are of course the exchange interaction

$-J \sum_i S_i S_{i+1}$, which is responsible for the occurrence of the phase transitions, and the external field term $-H \sum_i S_i$. The presence of

an external field will produce, through this term, a non-zero value of M at any temperature. If only these terms were present we would have an ordinary Ising model, and the complexities of the first-order transition would not be present. For this spin-one system, however, we must consider the additional order parameter $Q = \langle S_i^2 \rangle$. (Sometimes the parameter is written as $\langle S_i^2 \rangle - 2/3$. The $2/3$ is subtracted so that the trace of the operator is zero; this makes its high temperature average equal to zero.) Q (for "quadrupolar" order) is affected directly by the Δ term in the Hamiltonian; indeed Δ plays the role of an external field to Q in the same way that H does with M . The main point to notice about the order parameters is that they are not completely independent of one another. It is not possible, for example, to have a state of the system in which $M = 1$ and $Q = 0$, since $M = 1$ requires that all the spins have $S_i = +1$ which in turn produces $Q = 1$. The order parameters can thus be called kinematically coupled in that, even in the absence of any interaction, there are constraints on the values which can be taken on by the two together. This kinematical coupling produces an indirect effect by the term $\Delta \sum_i S_i^2$ on the

order parameter M . In fact, the presence of terms in the Hamiltonian which affect two kinematically coupled order parameters produces a competition between them which is ultimately responsible for the appearance of tricritical points, triple points, first-order transitions, etc. We can understand, on this basis, the change in the ground state from ferromagnetic to non-magnetic (for $H = 0$) with increasing Δ . The exchange term in (1) gives a lower energy for $M = 1$, while the crystal field term favors $Q = 0$. These two values are incompatible, however. The increase in Δ ultimately makes it more favorable energetically to have $Q = 0$ (which requires $M = 0$) than $M = 1$.

III. EFFECT OF A MAGNETIC FIELD

To see the full reasoning behind the name "tricritical" point we consider the effect of the magnetic field in (1) on the phase diagram in figure 1. Following Griffiths, we draw the phase diagram in a T - Δ - H space by adding an H -axis normal to the T and Δ axes in figure 1. The resulting phase diagram is shown in figure 2, and in the remainder of this section we give a qualitative discussion of the new features produced by the external magnetic field. At $T = 0$ it is clear that the external field is in competition with the field Δ . For $H = 0$ there is, as we have seen, a point, with increasing Δ , at which the ground state changes from $M = 1, Q = 1$ to $M = 0, Q = 0$.

Figure 2. Phase diagram in T - Δ - H space, showing the tricritical point as the intersection of three lines of critical points.

The presence of an external field favors the $M = 1$ ground state so that, for non-zero H , this state will persist for higher values of Δ . This effect leads to the presence of the wings in figure 2. There are three surfaces in T - Δ - H space. The upper edges of each of these surfaces is a line of critical points, and these three lines meet at the tricritical point A , suggesting its name.

The meaning of the surfaces can be seen by plotting the order parameter M as a function of H for different paths which cross these surfaces. Whenever the path crosses one of the surfaces, there is a discontinuity in the order parameter, and when the path goes through one of the lines of critical points the order parameter has an infinite slope.

In figure 3 we show M versus H for the paths aa , bb , cc , dd in figure 2. For large positive values of H the magnetization

Figure 3. M versus H for the paths aa , bb , cc , dd of figure 2.

is saturated. At $T = 0$ (path aa) the magnetization remains saturated, but jumps discontinuously in direction when the sign of the field changes from positive to negative. At higher temperatures, the magnetization decreases with decreasing H before undergoing a discontinuous jump. At the Curie temperature (path cc) the slope of M versus H is infinite at zero field. Finally, for $T > T_c$ (path dd) M varies smoothly through $H = 0$.

The meaning of the wings becomes clear if we proceed similarly. In figure 4 we show M versus H for the four paths $a'a'$, $b'b'$, $c'c'$, $d'd'$ in figure 2. For $T = 0$ and $H = 0$, the ground state of the system is non-magnetic, with $M = 0$ and $Q = 0$. Hence the M - H curves vary smoothly through $H = 0$. Here too, for very large H , the magnetization is saturated, and the discontinuities take place along the wings. The critical temperature produces an M - H curve as in path $c'c'$, with infinite slope occurring. The wings are symmetric in positive and negative H , as shown.

IV. DISCUSSION

The picture given above is applicable to many systems besides the theoretical model considered. That model was applied to the

Figure 4. M versus H for the paths $a'a'$, $b'b'$, $c'c'$, $d'd'$ in figure 2.

description of tricritical phenomena in mixtures of He^3 and He^4 .¹¹ The quantity Δ is then to be interpreted as the difference of the He^3 and He^4 chemical potentials, while the order parameter Q is $1 - x$, where x is the concentration of He^3 . The order parameter M is the condensate wave function $\langle\psi\rangle$, and H is a physically non-accessible field n which, if applied to the system, would produce superfluidity. Similar phenomena can be found in antiferromagnets, where $\Delta \rightarrow H$, $Q \rightarrow M$, $M \rightarrow M_s$, and $H \rightarrow H_s$. Here H and M are the external field and magnetization, while M_s and H_s are the staggered magnetization and staggered field, respectively. Tricritical phenomena also occur in structural phase transitions, and a full description of experiments on NH_4Cl is given in the next paper.¹²

Theoretical developments have followed the path of the theories of ordinary critical points. Landau and mean field theories were of course the first to be worked out,¹³ and they showed the change in critical indices at the tricritical point. Scaling theories have been also proposed¹³⁻¹⁵ and the usual scaling laws are expected to hold at the tricritical point, with allowance for the changed indices. The indices are found to be:

	<u>Mean Field</u>	<u>Tricritical (Mean Field)</u>	<u>3d Ising</u>
α	0	1/2	"1/3"
β	1/2	1/4	"5/16"
γ	1	1	5/4
δ	3	5	5

Energy scaling, which predicts $\alpha + 2\beta + \gamma = 2$, holds for all three examples. Perhaps the most important development in the recent activity in critical phenomena has been the application of Wilson's renormalization group approach¹⁶ to the tricritical point by Riedel and Wegner.¹⁷ They show that the mean field indices should be correct, with logarithmic corrections, for tricritical points in three dimensions. Experimental tests of this result are clearly desirable.

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