1876 (1972).

7

- <sup>15</sup>E. A. Turov and V. G. Shavrov, Fiz. Tverd. Tela
- 7, 217 (1965) [Sov. Phys. Solid State 7, 166 (1965)]. <sup>16</sup>C. Kittel, Phys. Rev. <u>110</u>, 836 (1958).

<sup>17</sup>A. I. Akhiezer, V. G. Bar'yakhtar, and M. I. Kaganov, Usp. Fiz. Nauk 71, 533 (1960) [Sov. Phys. Usp. 3, 567 (1961)].

- <sup>18</sup>J. Jensen, Intern. J. Magnetism <u>1</u>, 271 (1971).
- <sup>19</sup>D. T. Vigren and S. H. Liu, Phys. Rev. B <u>5</u>, 2719 (1972).
- <sup>20</sup>A. H. Nayyar and D. Sherrington, J. Phys. F. 2, 893 (1972).

<sup>21</sup>S. B. Palmer and E. W. Lee, Proc. Roy. Soc. (London) A327, 519 (1972).

<sup>22</sup>M. Long, A. R. Wazzan, and R. Stern, Phys. Rev.

 $\frac{178}{^{23}}$ L. M. Levinson and S. Shtrikman, J. Phys. Chem. Solids 32, 981 (1971).

<sup>24</sup>T. J. Moran and B. Lüthi, J. Phys. Chem. Solids <u>31</u>, 1735 (1970). <sup>25</sup>W. P. Mason, Phys. Rev. <u>96</u>, 302 (1954).

<sup>26</sup>F. Freyne, Phys. Rev. B <u>5</u>, 1327 (1972).

<sup>27</sup>H. B. Callen and E. Callen, J. Phys. Chem. Solids 27, 1271 (1966).

<sup>28</sup>J-L. Feron, G. Hug, and R. Pauthenet, Les Eléments des Terres Rares (Centre Nationale de la Re-

cherche Scientifique, 1970), Vol. 2, p. 19.

<sup>29</sup>C. D. Graham, Jr., General Electric Report No. 66-C-218, 1966 (unpublished).

<sup>30</sup>M. S. S. Brooks and D. A. Goodings, J. Phys. C <u>1</u>, 1279 (1968).

<sup>31</sup>C. D. Graham, Jr., J. Appl. Phys. <u>38</u>, 1375 (1967).

<sup>32</sup>J. J. Rhyne and A. E. Clark, J. Appl. Phys. 38, 1379 (1967).

<sup>33</sup>J. J. Rhyne, S. Foner, E. J. McNiff, Jr., and R. Doclo, J. Appl. Phys. 39, 892 (1968).

<sup>34</sup>R. M. Bozorth, A. E. Clark, and R. J. Gambino, in Proceedings of the Eleventh International Conference on Low-Temperature Physics, St. Andrews (St. Andrews

Printing Dept., St. Andrews, Scotland, 1968), p. 1106.

<sup>35</sup>R. M. Bozorth, A. E. Clark, and J. H. Van Vleck, Intern. J. Magnetism 2, 19 (1972).

<sup>36</sup>E. S. Fisher and D. Dever, in Proceedings of the Oak Ridge Conference on Rare Earths, 1968 (unpublished),

p. 522. <sup>37</sup>R. J. Pollina and B. Lüthi, Phys. Rev. <u>177</u>, 841 (1969).

<sup>38</sup>M. Rosen and H. Klimker, Phys. Rev. B 1, 3748 (1970).

<sup>39</sup>E. S. Fisher and D. Dever, Trans. Met. Soc. AIME <u>239</u>, 48 (1967).

 $\overline{}^{40}$ J. Alstad and S. Legvold, J. Appl. Phys. <u>35</u>, 1752 (1964).

<sup>41</sup>P. de V. Du Plessis, Phil. Mag. 18, 145 (1968).

<sup>42</sup>A. E. Clark, B. F. DeSavage, and R. Bozorth, Phys. Rev. 138, A216 (1965).

<sup>43</sup>B. R. Cooper, Phys. Rev. <u>169</u>, 281 (1968).

<sup>44</sup>M. Rosen, Phys. Rev. Letters <u>19</u>, 695 (1967).

<sup>45</sup>J. J. Rhyne and S. Legvold, Phys. Rev. <u>138</u>, A507 (1965).

<sup>46</sup>J. J. Rhyne, S. Legvold, and E. T. Rodine, Phys. Rev. 154, 266 (1967).

<sup>47</sup>J. J. Rhyne and S. Legvold, Phys. Rev. <u>140</u>, A2143 (1965).

PHYSICAL REVIEW B

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# **Proposal for Notation at Tricritical Points**\*

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A notation for critical exponents at a tricritical point is proposed on the basis that the line of critical points observed experimentally in metamagnets,  $NH_4Cl$ , or  $He^3$ - $He^4$  mixtures defines a special direction in the space of thermodynamic parameters. Scaling at a tricritical point implies certain relations among the exponents which are summarized in a table.

# I. INTRODUCTION

At the present time there is a well-developed phenomenological description of ordinary ferromagnetic and liquid-vapor critical points in terms of exponents and scaling, <sup>1</sup> and this phenomenology can be extended fairly easily<sup>2,3</sup> to lines and surfaces of critical points (which arise, for example, in antiferromagnets, fluid mixtures, and liquid He<sup>4</sup>) wherever the ideas of "smoothness"<sup>3</sup> or "universality"<sup>4</sup> are applicable. Probably the simplest situation at which smoothness and, hence, the conventional description of critical points breaks down is at a tricritical point,<sup>5</sup> and consequently tricritical points have recently been the subject of several experimental and theoretical investigations. 6-8

As might be expected a rather diverse notation for tricritical exponents has been employed by different authors. The purpose of this paper is to suggest a notation which is a logical extension to tricritical points of the notation for exponents which is already in use at "ordinary" critical points and at the same time maintains certain essential distinctions which arise at tricritical points and which lead to confusion if ignored. More important, we wish to suggest a point of view closely allied with (and, in fact, an extension of) the geometrical analysis set forth in an earlier paper.<sup>2</sup> Scientists

who do not care for our notation (which follows fairly closely that of Riedel, <sup>6</sup> with some changes and a number of explanatory comments) may still find the geometrical point of view helpful in explaining their own notation and, thus, avoiding confusion on the part of the reader.

Our discussion is limited to a particular type of tricritical point (more details are given below in Sec. II), which corresponds (we believe) to experimental observations on certain metamagnets,  $NH_4Cl$ , and  $He^3-He^4$  mixtures. There may well be other tricritical points where the geometrical relations are somewhat different and where the discussion given below is inapplicable.

## **II. THERMODYNAMIC VARIABLES AT A TRICRITICAL POINT**

We shall, to be specific, consider a tricritical point in a metamagnet. The same sort of description is, however, possible for NH<sub>4</sub>Cl and He<sup>3</sup>-He<sup>4</sup> mixtures, with a suitable change of variables. Let H be the internal<sup>9</sup> magnetic field in the metamagnet and M its thermodynamic conjugate, the average magnetization. The following discussion applies to NH<sub>4</sub>Cl with H replaced by -p (pressure)<sup>10</sup> and Mreplaced by V (volume), and to He<sup>3</sup>-He<sup>4</sup> mixtures under constant pressure<sup>11</sup> with H replaced by  $\mu_3$ - $\mu_4$ (chemical potentials for the two isotopes) and Mby  $x_3$  (fractional molar concentration of He<sup>3</sup>). In all cases, S is the entropy, T the temperature,  $\psi$ the order parameter, and  $\zeta$  its thermodynamic conjugate (see the following).

The observable characteristic of experimental systems believed to possess tricritical points is that a first-order phase-transition line in the space of thermodynamic "fields" (variables such as temperature and pressure which are the same in two phases coexisting in equilibrium) changes into a single  $\lambda$  line or line of critical points.<sup>12</sup> The point separating the first-order line from the critical line is the tricritical point (see Fig. 1).

It is convenient for conceptual purposes to imagine a field  $\zeta$  which couples to the order parameter  $\psi$  associated with the critical line and is the analog of a magnetic field for a ferromagnet. In a metamagnet  $\psi$  is the sublattice magnetization and  $\zeta$  an appropriate "staggered" magnetic field. In helium mixtures  $\psi$  is the superfluid order parameter and



FIG. 1. Phase diagram for a metamagnet showing a tricritical point (dot) at the junction of a first-order transition (solid curve) and a  $\lambda$  line or line of critical points (dashed curve). The straight line through the tricritical point defines the function  $H_1(T)$ , or  $T_1(H)$ .



FIG. 2. Phase diagram for a metamagnet in the  $(\xi, T, H)$  space. Cross hatching indicates coexistence surfaces and the dashed lines are critical lines.

in NH<sub>4</sub>Cl it is the fraction of ammonia ions having one orientation minus the fraction having the other orientation. In the last two cases the field  $\zeta$  is more difficult to visualize but may be defined as the thermodynamic conjugate of  $\psi$ . In all the cases mentioned,  $\zeta$  is a "fictitious" field unavailable in the laboratory, but nonetheless a valuable conceptual tool to relate the experimentally observed phase transitions to the critical phenomena observed in simple ferromagnets and fluids.

Based on approximate model calculations it is conjectured that the phase diagram of a metamagnet would look something like Fig. 2 in the  $(T, H, \zeta)$  space. A first-order coexistence surface at  $\zeta = 0$  (on which  $\psi$  changes discontinuously as  $\zeta$ goes from positive to negative values) bifurcates for *H* sufficiently large into two coexistence surfaces or "wings" projecting in a symmetrical fashion into the regions  $\zeta > 0$  and  $\zeta < 0$ . From this point of view the first-order line of Fig. 1 is seen as a line of triple points. In the remainder of the paper we shall focus attention on region  $\zeta = 0$  and ignore the wings and the corresponding critical lines at nonzero  $\zeta$ .

The thermodynamic properties can be expressed in terms of a free energy  $F(\zeta, T, H)$  and its derivatives; in particular,

$$\psi = -\frac{\partial F}{\partial \xi} , \qquad (2.1)$$

$$S = -\frac{\partial F}{\partial T}, \qquad (2.2)$$

$$M = -\frac{\partial F}{\partial H} \quad . \tag{2.3}$$

#### **III. CRITICAL AND TRICRITICAL EXPONENTS**

Let us first consider the critical exponents along the critical line in the  $\zeta = 0$  plane, shown in Fig. 1. Let *P* be a plane parallel to the  $\zeta$  and *T* axes (Fig. 2) passing through a point *B* on this line. The projection of *P* on the (*H*, *T*) plane is the line pp' in Fig. 3. The plane *P* intersects the coexis-



FIG. 3. Projections on the (H, T) plane of the planes P'(pp') and Q'(qq') passing through the point B on the critical line.

tence surface at  $\zeta = 0$  in a line and the line of critical points in the single point *B* at a temperature  $T_B$ , as shown in Fig. 4(a). On *P* we have a situation analogous to that in simple ferromagnets, with  $\zeta$ playing the role of a magnetic field, and by analogy we can make the customary identification of critical indices along the line  $\zeta = 0$ :

$$\psi_0 \sim (T_B - T)^{\beta}$$
, (3.1a)

$$\frac{\partial \psi}{\partial \zeta} \sim (T - T_B)^{-\gamma}$$
, (3.1b)

$$\frac{\partial S}{\partial T} \sim (T - T_B)^{-\alpha} \quad , \qquad (3.1c)$$

etc., where  $\psi_0$  denotes the spontaneous nonzero value of the order parameter<sup>13</sup> obtained as  $\zeta \rightarrow 0+$ . Similarly, the correlation function for the order parameter

$$\Gamma(\vec{\mathbf{r}}) = \langle \psi(\mathbf{0})\psi(\vec{\mathbf{r}})\rangle - \langle \psi(\mathbf{0})\rangle \langle \psi(\vec{\mathbf{r}})\rangle$$
(3.2)

is expected to decay as<sup>14</sup>

$$\Gamma \sim \left| \vec{\mathbf{r}} \right|^{-(d-2+\eta)} \tag{3.1d}$$

for large  $|\vec{\mathbf{r}}|$  and  $T = T_B$ ; here *d* is the dimensionality (three for the systems of experimental interest). Away from the critical point,  $\Gamma$  should decay with a correlation length  $\xi$  which varies as

$$\xi \sim (T - T_B)^{-\nu}$$
 . (3.1e)

Of course, for  $T < T_B$  the exponents  $\alpha$ ,  $\gamma$ , and  $\nu$  should (if different from the corresponding indices for  $T > T_B$ ) be denoted by  $\alpha'$ ,  $\gamma'$ ,  $\nu'$ .

Of these exponents, only  $\alpha$  and  $\alpha'$  can be obtained by direct thermodynamic measurements. The others can be obtained from neutron diffraction in the case of metamagnets and NH<sub>4</sub>Cl. The exponent  $\delta$  defined by

$$\boldsymbol{\zeta} \sim \boldsymbol{\psi}^{\delta} \tag{3.1f}$$

for  $T = T_B$  is not accessible to direct measurement but, along with  $\Delta = \beta \delta$ , plays a role in scaling theories. According to current phenomenological ideas (Pippard relations<sup>15</sup> or "smoothness"), precisely the same exponents should be obtained if one uses in place of P a plane Q parallel to the H and  $\zeta$  axes (Fig. 2) passing through the point B. The projection of Q in the (H, T) plane is the line qq' in Fig. 3, and the phase diagram in the plane Q is shown in Fig. 4(b). Using the same analogy as before we write

$$\psi_0 \sim (H_B - H)^{\beta}$$
, (3.3a)

$$\frac{\partial \psi}{\partial \zeta} \sim (H - H_B)^{-\gamma}$$
, (3.3b)

$$\frac{\partial M}{\partial H} \sim (H - H_B)^{-\alpha} , \qquad (3.3c)$$

and corresponding results for other quantities.

The equality of the exponents in (3.1) and (3.3) depends, from a geometrical point of view, on the fact that the critical line at *B* is parallel to neither the *T* nor the *H* axis. However, it may turn out in practice that even though the critical line is not precisely parallel to either axis, it is "sufficiently" parallel so that one plane is, for practical purposes, to be preferred to the other. Thus for *B* a point on the critical line with *H* very small, the *P* plane will be the better choice because the critical line is parallel to the *H* axis at H=0.

The tricritical exponents, which we denote using a subscript t, <sup>16</sup> can be defined in the same way by passing a P plane or a Q plane through the tricritical point. Let us, for purposes of illustration, assume the latter. Then at  $T = T_t$  (tricritical temperature) and  $\zeta = 0$  we have

$$\psi_0 \sim (H_t - H)^{\beta_t}$$
, (3.4a)

$$\frac{\partial \psi}{\partial \zeta} \sim (H - H_t)^{-\gamma_t} , \qquad (3.4b)$$



FIG. 4. Phase diagram on (a) the plane P and (b) the plane Q. Solid lines are coexistence lines which terminate at the critical point B.

$$\frac{\partial M}{\partial H} \sim (H - H_t)^{-\alpha_t} \quad , \qquad (3.4c)$$

$$\xi \sim (H - H_t)^{-\nu_t}$$
, (3.4d)

and for  $H = H_t$  (tricritical field) as well as  $T = T_t$ ,

$$\mathbf{\Gamma} \sim \left| \dot{\mathbf{r}} \right|^{-(d-2+\eta_t)} , \qquad (3.4e)$$

$$\boldsymbol{\zeta} \sim \boldsymbol{\psi}^{\boldsymbol{\delta}_t} \quad . \tag{3.4f}$$

For  $H < H_t$ , we have corresponding indices  $\alpha'_t$ ,  $\gamma'_t$ ,  $\nu'_t$ . Alternatively, of course, one can let  $H = H_t$  and define the indices with  $T - T_t$  replacing  $H - H_t$ , e.g.,

$$\psi_0 \sim (T_t - T)^{\beta_t} \quad , \tag{3.5}$$

etc.

From the viewpoint of Ref. 2 (suitably extended), one would expect the two sets of indices, those in (3.4) and (3.5), to be the same provided the critical line and the first-order line are not parallel to either the H or the T axis. We shall in the subsequent discussion assume that the first-order line and the critical line are asymptotically parallel at the tricritical point in the (H, T) plane. Needless to say, an experimental check of these ideas would be very valuable. Also one must be cautious because in practice the critical line may be sufficiently parallel to either the T or the H axis so that one type of plane is to be preferred over the other in defining exponents. For example, if the critical line is (in some sense) almost parallel to the Taxis, the definitions in (3.4) are preferable to those in (3.5).

The exponents defined above obviously come about by regarding the tricritical point as a particular point on the line of critical points. An alternative set of exponents, which we might call "subsidiary tricritical exponents," comes about if one regards the tricritical point as the terminus of the line of first-order phase transitions in the (H, T)plane (Fig. 1), in analogy with an "ordinary" critical point. This is the point of view adopted by Goellner and Meyer.<sup>7</sup> We shall denote the corresponding exponents with a subscript u.

Thus *M* has a discontinuity  $\Delta M$  across the first-order curve, and we define  $\beta_u$  by

$$\Delta M \sim (T_t - T)^{\beta u} \quad . \tag{3.6a}$$

It may turn out that this discontinuity is actually asymmetric in the sense that if we let  $M_{+}$  be the value of M in the disordered phase ( $\psi_{0} = 0$ ) along the first-order curve and  $M_{-}$  the value in the ordered phase ( $\psi_{0} > 0$ ), there are two distinct exponents  $\beta_{+}$  and  $\beta_{-}$  such that<sup>17</sup>

$$\Delta M_{+} = M_{+} - M_{t} \sim (T_{t} - T)^{\beta_{+}} , \qquad (3.6b)$$

$$\Delta M_{-} = M_{t} - M_{-} \sim (T_{t} - T)^{\beta_{-}} , \qquad (3.6c)$$

where  $M_t$  is the tricritical value of M. One may hope that this asymmetry is not present in physical systems (and it is ruled out if scaling applies at the tricritical point), but the matter should be checked experimentally, and one may wish to use a notation which allows for this difference.

Along the line  $M = M_t$ ,  $T > T_t$ , we suppose that

$$\frac{\partial M}{\partial H} \sim (T - T_t)^{-\gamma_u} \quad , \tag{3.6d}$$

whereas for  $T < T_t$  along the first-order line,

$$\frac{\partial M}{\partial H} \sim (T_t - T)^{-r_u} \quad . \tag{3.6e}$$

The index  $\alpha_n$  is defined by

$$\frac{C_M}{T} = \left(\frac{\partial S}{\partial T}\right)_{M=M_t} \sim (T - T_t)^{-\alpha} u \qquad (3.6f)$$

with an index  $\alpha'_u$  for  $T < T_t$ . In the case where  $\alpha_u$ and  $\alpha'_u$  are negative, one is to suppose that  $C_M$  has a smooth part plus a singular part, and only the variation of the latter is given by (3.6f). At  $T = T_t$ we write

$$\left| H - H_t \right| \sim \left| M - M_t \right|^{\delta_u} \quad . \tag{3.6g}$$

In the case of  $\gamma'_u$  and  $\delta_u$  it is possible, just as in the case of  $\beta_u$ , that different exponents will occur for the disordered and ordered phases. In this case,  $\gamma'_u$  should be replaced by  $\gamma'_{\star}$ ,  $\gamma'_{\star}$ , and  $\delta_u$  by  $\delta_{\star}$ ,  $\delta_{-}$ , where the subscript (+) refers to the disordered ( $\psi_0 = 0$ ) and (-) to the ordered phase.

There should also be subsidiary exponents associated with the correlation function

$$\Gamma_{u}(\vec{\mathbf{r}}) = \langle M(\vec{\mathbf{r}})M(0) \rangle - \langle M(\vec{\mathbf{r}}) \rangle \langle M(0) \rangle \quad . \tag{3.7}$$

Thus at the tricritical point itself, one may suppose that  $^{14}\,$ 

$$\Gamma_{u} \sim \left| \vec{r} \right|^{-(d-2+\eta_{u})} , \qquad (3.6h)$$

while away from the tricritical point  $\Gamma$  decays with a correlation length  $\xi_u$ , and for  $M = M_t$ ,

$$\xi_{u} \sim (T - T_{t})^{-\nu_{u}} , \qquad (3.6i)$$

while for  $T < T_t$  along the first-order line,

$$\xi_{u} \sim (T_{t} - T)^{-\nu_{u}^{\prime}} \quad , \qquad (3.6j)$$

and it may be necessary to distinguish  $\nu'_{+}$  and  $\nu'_{-}$ .

One may hope that the situation will turn out to be relatively simple and that  $\nu'_{+} = \nu'_{-} (=\nu'_{u}) = \nu_{u}$ . In addition, if away from the critical (and tricritical) points the system is characterized by a single length—a prime ingredient of current scaling theories—one would expect

$$\xi_{u} \simeq \xi \tag{3.8}$$

(or at least the H and T dependence should be simi-

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TABLE I. Relationships among tricritical exponents implied by scaling. Note: The most concise summary of relationships between exponents is provided by expressing them all in terms of a small "canonical" set of exponents which we have chosen as  $\alpha_t$ ,  $\beta_t$ ,  $\phi = 1/\varphi_t$ , and  $\nu_t$ . Many other relationships can be derived from these, and it is helpful to note that the exponents with a particular subscript satisfy the "usual" scaling relations among themselves, e.g.,  $\alpha_t + 2\beta_t + \gamma_t = 2$ ;  $\gamma_u = \beta_u(\delta_u - 1)$ , etc.

$\gamma_t = 2 - \alpha_t - 2\beta_t$	$\gamma_{\mu} = \gamma_{+}' = \gamma_{-}' = \phi \alpha_{t}$
$\delta_t = -1 + (2 - \alpha_t) / \beta_t$	$\delta_u = \delta_+ = \delta = 1/(1 - \alpha_t)$
$\Delta_t = \beta_t \delta_t = 2 - \alpha_t - \beta_t$	$\Delta_{u} = \phi$
$\varphi_t = 1/\phi$	$2 - \eta_t = (2 - \alpha_t - 2\beta_t) / \nu_t$
$\alpha_u = 2 - \phi \left(2 - \alpha_t\right)$	$\nu_u = \nu_+ = \nu = \phi \nu_t$
$\beta_u = \beta_+ = \beta = \phi \left(1 - \alpha_t\right)$	$2 - \eta_u = \alpha_t / \nu_t$

lar). Even if (3.8) is correct, it does *not* follow that  $\nu_u = \nu_t$ , since these exponents refer to different paths in the (H, T) plane. The two are related by the crossover exponent  $\phi$  if tricritical point scaling is valid (Sec. IV and Table I).

The choice of  $|T - T_t|$  as a variable measuring "distance" from the critical point in our discussion of subsidiary exponents is, from the point of view of Ref. 2, somewhat arbitrary. Under the assumption that the line of critical points is not parallel to the *H* axis at the tricritical point, one could equally well employ  $|H - H_t|$ , or some combination of *H* and *T*.

### IV. SCALING AT THE TRICRITICAL POINT

There have been various proposals<sup>5, 6, 8</sup> for scaling at a tricritical point. The scheme we adopt here (which leans heavily on the ideas of Riedel<sup>6</sup> and Hankey *et al.*<sup>8</sup>) may not be optimal, but probably gives the same relationship among the exponents as any reasonable scaling proposal.

First we must introduce suitable coordinates. Let a straight line<sup>18</sup> through the tricritical point lying tangent to the line of critical points and the first-order line in the (H, T) plane (Fig. 1) define the function  $H_1(T)$  or, alternatively, the function  $T_1(H)$ . Introduce the variables g and  $\lambda$  by

$$g = H - H_1(T)$$
, (4.1a)

$$\lambda = T - T_t \quad , \tag{4.1b}$$

which, together with  $\xi$ , shall serve as a coordinate system near the tricritical point. Note that the  $\xi$ axis cuts the (H, T) plane containing the coexistence surface shown in Fig. 2, while the g axis (i.e., the line  $\lambda = 0$ ,  $\xi = 0$ ) cuts the critical line but lies in the (H, T) plane, and the  $\lambda$  axis (g=0) lies parallel to the critical line at the tricritical point. This is a sensible choice of axes from the geometrical perspective of Ref. 2, but is certainly not unique. In particular, an alternate choice is

$$g = T - T_1(H)$$
, (4.2a)

$$\lambda = H - H_t \quad , \tag{4.2b}$$

which leads to the same geometrical properties, but with the g axis now parallel to the T axis. And, obviously, there are other choices in which the g axis is parallel to neither the H axis nor the T axis. It should be noted that this ambiguity makes no difference in the exponent relations obtained below provided the crossover exponent  $\phi$  is greater than one ( $\varphi_t$  is less than one). It may well be that there is an optimum choice for the direction of the g axis in the sense that corrections to the scaling part of the singular free energy are minimized but there is no way of estimating this direction a priori (and there is no reason to assume it will be "perpendicular" to the  $\lambda$  axis with some arbitrary normalization of the H and T coordinates).

Let us assume that suitable coordinates have been chosen [e.g., (4.1) or (4.2)]. The scaling assumption for the free energy is that it can be written as the sum of two terms, a regular and a singular part:

$$F = F_r + F_s \quad , \tag{4.3}$$

and that the latter satisfies a functional equation:

$$F_{s}(l\lambda, l^{\phi}g, l^{\phi\Delta_{t}}\zeta) = l^{\phi(2-\alpha_{t})}F_{s}(\lambda, g, \zeta) \qquad (4.4a)$$

for all values of the real positive parameter l, provided the arguments of  $F_s$  (on *both* sides of the equation) are sufficiently small; i.e., (4.4a) is supposed to be valid in some sense asymptotically close to the tricritical point.<sup>19</sup> The function  $F_r$  is usually assumed to be analytic or, at least, to have continuous partial derivatives of sufficiently high order that it makes no contribution to the singular behavior of the quantities of interest. Here  $\phi$  is a crossover exponent related to Riedel's<sup>6</sup>  $\varphi_r$  by

$$\phi = 1/\varphi_t \quad , \tag{4.5}$$

and  $\Delta_t = \beta_t \delta_t$ . There is some ambiguity in the literature as to the definition of "the" crossover exponent.<sup>20</sup> For cases of interest to us  $\phi$  will be larger than one and  $\varphi_t$  less than one and in terms of  $\varphi_t$  as crossover exponent, the functional equation (4.4a) assumes the form

$$F_{s}(l^{\varphi}t\lambda, lg, l^{\Delta}t\zeta) = l^{2-\alpha}tF_{s}(\lambda, g, \zeta) \quad . \tag{4.4b}$$

Among the consequences of (4.4) is the result that both the first-order line and the critical line in Fig. 1 have the functional form, asymptotically close to the tricritical point, of

$$g = \operatorname{const} \times \lambda^{\phi}$$
, (4.6)

where the constant is, in general, different in the two cases. Note that  $\phi > 1$  is necessary so that the first-order line and the critical line are asymptotically parallel in the (H, T) plane.

For  $\lambda = 0$ , (4.4) implies that ordinary scaling occurs at the tricritical point, so that the tricritical exponents may be expressed in terms of  $\alpha_t$  and  $\Delta_t$ , as in Table I. In addition, (4.4) permits one to express the exponents  $\alpha_{\mu}$ ,  $\gamma_{\mu}$ , etc., in terms of  $\phi$ and  $\alpha_t$ , and the results are given in Table I.<sup>21</sup> All the relations assume  $\phi > 1$ ;  $\phi \leq 1$  would indicate a geometrical situation different from that sketched in Fig. 1 and thus necessitate a different analysis.

One can make an analogous scaling assumption for the correlation functions. We here restrict ourselves to the pair functions  $\Gamma$  and  $\Gamma_{\mu}$  introduced in (3.2) and (3.7), which are probably the ones of greatest interest in scattering experiments. Assuming that  $\lambda$ , g, and  $\zeta$  are sufficiently small and that  $|\vec{\mathbf{r}}|$  is sufficiently large, the appropriate functional relationships are

$$\Gamma(l\lambda, l^{\phi}g, l^{\phi\Delta t}\zeta; l^{-\phi\nu t}\mathbf{r})$$

$$= l^{\phi \nu_t (d-2+\eta_t)} \Gamma(\lambda, g, \zeta; \vec{r}) , \quad (4.7)$$

 $\Gamma_u(l\lambda, l^{\phi}g, l^{\phi\Delta_t}\zeta; l^{-\nu_u}\mathbf{r})$ 

$$= l^{\nu_u (d-2+\eta_u)} \Gamma_u (\lambda, g, \zeta; \vec{r}) , \quad (4.8)$$

assumed valid for all positive l.

Upon integration of the appropriate fluctuation relations<sup>22</sup> one obtains the usual relationship between  $\nu$ ,  $\eta$ , and  $\gamma$ :

$$\gamma_t = (2 - \eta_t)\nu_t$$
,  $\gamma_u = (2 - \eta_u)\nu_u$ . (4.9)

If in addition one assumes that (3.8) is valid, it follows that

$$\nu_u = \phi \nu_t \quad . \tag{4.10}$$

If the scaling approach [including (4.8) and (4.9)] is valid, we can conclude that in addition to the exponents along the critical line ( $\alpha$ ,  $\beta$ ,  $\gamma$ , etc.) only

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- <sup>1</sup>See, for example, M. E. Fisher, Rept. Progr. Phys.  $\frac{30}{^2}$ R. B. Griffiths and J. C. Wheeler, Phys. Rev. A <u>2</u>,
- 1047 (1970).

<sup>3</sup>B. J. Lipa and M. J. Buckingham, Phys. Letters 26A, 643 (1968); M. E. Fisher, Phys. Rev. 176, 257 (1968); R. B. Griffiths, Phys. Rev. Letters 24, 1479 (1970), and in Critical Phenomena in Alloys, Magnets, and Superconductors, edited by R. E. Mills, E. Ascher, and R. I. Jaffee (McGraw-Hill, New York, 1971), p. 377.

<sup>4</sup>L. P. Kadanoff, in Proceedings of the Enrico Fermi Summer School of Physics, Varenna, 1970, edited by M. S. Green (Academic, New York, to be published); P. G. Watson, J. Phys. C 2, 1883 (1969); 2, 2158 (1969); D. D. Betts, A. J. Guttmann, and G. S. Joyce, *ibid.* <u>4</u>, 1994 (1971).

<sup>5</sup>R. B. Griffiths, Phys. Rev. Letters 24, 715 (1970).

<sup>6</sup>E. K. Riedel, Phys. Rev. Letters <u>28</u>, 675 (1972).

four additional exponents are needed at the tricritical point to describe the thermodynamic properties and the pair correlation function. In Table I we have used  $\alpha_t$ ,  $\beta_t$ ,  $\phi$  (or  $\varphi_t$ ), and  $\nu_t$ , and all the other exponents are expressed in terms of these.

# V. SUMMARY

On the basis of present phenomenological ideas there are at least three conceptually distinct sets of exponents in the physically accessible  $\zeta = 0$  plane near a tricritical point: (i) A set of exponents associated with the line of critical points away from the tricritical point, which we suggest be denoted by the usual Greek letters without a subscript: (ii) a set of exponents analogous to (i) obtained by considering the tricritical point as a special point on the line of critical points, for which we have used the usual Greek letters with a subscript t; and (iii) a set of exponents associated with the first-order line in the  $\zeta = 0$  plane, regarding the tricritical point at the terminus of this curve as analogous to an "ordinary" critical point-these we have designated with a subscript u. However, if scaling is valid at the tricritical point there is only one additional exponent in (iii) not contained in (ii), viz., the crossover exponent  $\phi$  or  $\varphi_{\star} = 1/\phi$ . The proposals set forth here depend on the assumption that the line of critical points defines a special direction at the tricritical point. They are tentative and may need to be revised in the light of further experimental and theoretical developments.

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<sup>7</sup>T. Alvesalo *et al.*, Phys. Rev. Letters 22, 1281 (1969); Phys. Rev. A 4, 2354 (1971); S. T. Islander and W. Zimmerman, Jr., ibid. (to be published); G. Goellner and H. Meyer, Phys. Rev. Letters 26, 1534 (1971); M. Blume, V. J. Emery, and R. B. Griffiths, Phys. Rev. A 4, 1071 (1971); O. K. Rice and D. R. Chang, ibid. 5, 1419 (1972); D. P. Landau et al., Phys. Rev. B 3, 2310 (1971); Phys. Rev. Letters 28, 449 (1972); C. W. Garland and B. B. Weiner, Phys. Rev. B 3, 1634 (1971); D. M. Saul and M. Wortis, in Magnetism and Magnetic Materials 1971, edited by C. D. Graham, Jr. and J. J. Rhyne (AIP, New York, 1972), p. 349; B. L. Arora and D. P. Landau, ibid., p. 352; L. Reatto, Phys. Rev. B 5, 204 (1972); E. K. Riedel and F. J. Wegner, Phys. Rev. Letters 29, 349 (1972); F. Harbus and H. E. Stanley, ibid. 29, 58 (1972); J. F. Nagle and J. C. Bonner, J. Chem. Phys. 54, 729 (1971); and J. C. Bonner and J. F. Nagle, J. Appl. Phys. 42, 1280 (1971). <sup>8</sup>A. Hankey, H. E. Stanley, and T. S. Chang, Phys.

Rev. Letters 29, 278 (1972). See also A. Hankey and H. E. Stanley, Phys. Rev. B <u>6</u>, 3515 (1972).

<sup>9</sup>The internal field is the applied magnetic field with a demagnetizing correction subtracted. It is equal to the applied field only for a specimen in the shape of a long thin needle placed parallel to the applied field.

<sup>10</sup>In NH<sub>4</sub>Cl the critical temperature is an increasing function of pressure and thus the ordered (low-temperature) phase lies on the high-pressure side of the critical line. This leads to certain minor changes in Sec. III and the correct formulas are obtained by replacing H by -p (thus  $H_t - H$  becomes  $p - p_t$ ).

<sup>11</sup>As a first approximation one can regard saturated vapor pressure as a constant pressure near the tricritical point.

<sup>12</sup>This is to be distinguished from the spin-flop transition in certain antiferromagnets where *two*  $\lambda$  lines and a first-order line meet at one point on the phase diagram.

<sup>13</sup>In superfluid helium,  $\psi$  is, in general, a complex quantity with both a magnitude and a phase. For our present purposes we may assume that both  $\psi$  and  $\zeta$  are real.

<sup>14</sup>The situation in certain metamagnets may be more complex than indicated here because of spatial anisotropy.

<sup>15</sup>A. B. Pippard, *Elements of Classical Thermodynamics* (Cambridge U. P., Cambridge, England, 1957), Chap. 9.

<sup>16</sup>Reidel, Ref. 6, places a dot over the critical exponent to indicate that it is defined with respect to a suitable "scaling field." Our approach, on the other hand, is to define exponents with respect to variables related in an appropriate way to the phase diagram. It seems quite likely that the two types of exponents are the same, but as long as this is in doubt the distinction may be conveniently maintained through the omission of dots from the exponents we define here.

<sup>17</sup>The reader may be surprised that we propose such a distinction when no asymmetry (of this type) has yet been observed at "ordinary" critical points in fluids. However, in the latter case the two coexisting phases are physically very similar near the critical point, whereas at tricritical points they are physically dissimilar:  $\psi_0$  is nonzero in one phase, but not in the other.

<sup>18</sup>One may wish in some circumstances to make  $H_1(T)$  a curved line, but such refinements are beyond the scope of this paper.

<sup>19</sup>It may be necessary to modify the simple power laws in (4.4) with additional logarithmic factors, as discussed by F. J. Wegner and E. K. Reidel, Phys. Rev. B (to be published). However, these will not alter the relations among the exponents implied by scaling.

<sup>20</sup>It seems to be customary in the case of interactions which reduce the symmetry or change the dimensionality to use a crossover exponent which is larger than one, and hence our choice of  $\phi$ . However, an equally good (perhaps better) case can be made for an exponent less than one, which is Riedel's choice in Ref. 6.

<sup>21</sup>In order to relate the subsidiary exponents for  $T > T_t$  to the tricritical exponents, it is necessary to assume that  $\beta_u \leq 2$  and  $\gamma_u > 0$ . These restrictions are needed to ensure that the curve  $M = M_t$  satisfies  $|g| \leq (\text{const})\lambda^{\phi}$ .

 $^{22}$ Certain subtleties arise due to noncommutativity of operators, but we shall assume that (4.9) is valid anyway.

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