Nonuniversality of Tricritical Behavior

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Deviations from the classical phenomenological theory of tricriticality are analyzed on the basis of the exact solution (in four field variables) of the spherical-model limit ($n \to \infty$) in three dimensions. The scaling functions are *nonuniversal* but are parametrized by a *single variable*, which vanishes for infinite-range interactions. Special relations between critical amplitude ratios correlate well with observations on antiferromagnets and ^{3}He-^{4}He mixtures. Novel qualitative predictions are made for the three-phase monohedron below T_t.

The universality of critical-point behavior is now a well-established concept: Not only should critical exponents be the same for all systems in a given class (defined by dimensionality, order-parameter symmetry, etc.), but dimensionless critical-amplitude ratios and the full scaling functions should also be invariant within a class. For ordinary critical points, universality is well checked by both experimental and theoretical studies. For *tricritical points*, however, the situation is less clear. Renormalization-group arguments[1] indicate that for *three-dimensional systems* (to which we restrict our considerations), the tricritical exponents should be classical ($\alpha = -1$, $\phi = 2$, $\Delta = \frac{5}{2}$, $\Delta_3 = \frac{3}{2}$),[2] although logarithmic factors in $t = (T - T_t)/T_t$ are anticipated for systems with order parameters of finitely many components ($n < \infty$).[1,3] The former conclusion is consistent with the best modern experiments although no logarithmic factors have yet been detected. But, even though observed tricritical exponents are classical, the behavior of real systems deviates in marked qualitative ways from other predictions of the classical phenomenological theories; see, e.g., Fig. 1. What is the significance of these deviations? How are the various deviations correlated with one another?

Here we report an initial attack on these questions, based on the recently achieved exact solution for tricritical behavior in the spherical-model or infinite-component limit ($n \to \infty$).[4,5] In this limit the exponents are classical but the observed deviations (and others yet to be seen) do, indeed, occur. However, despite earlier expectations, they are *not* universal in magnitude! Nevertheless, the asymptotic nonuniversality is completely parametrized by a single variable, $z \propto (a/R_0)^3$, where R_0 measures the range of interactions relative to a microscopic length a.

The full description of tricritical behavior[2] requires, in addition to the temperature $T = T_t(1+t)$, three fields h_j ($j = 1, 2, 3$) and their conjugate densities m_j. In a model with spin variables s, one may take $m_j \equiv \langle s^j \rangle$. More concretely, $m_1 \equiv m$, the primary order parameter, corresponds to the staggered magnetization $M^\dagger$ in an antiferromagnet, or to the wave-function operator $\hat{\psi}$ in helium three-four mixtures. The "even" density $-m_2$ then corresponds, respectively, to M, the ordinary magnetization, or to x_4, the ^{4}He mole fraction; the conjugate field h_2 is the magnetic field H or chemical potential difference $\Delta = \mu_3 - \mu_4$. The additional "odd" density m_3 fluctuates independently of m and m_2 in the tricritical region but is harder to identify microscopically except in the case of ordinary fluid mixtures. Here all three m_j correspond, asymptotically, to independent linear combinations of the three or more mole fractions x_k (or densities ρ_k)[6,7]; the h_i are appropriate linear combinations of the chemical potentials μ_k.

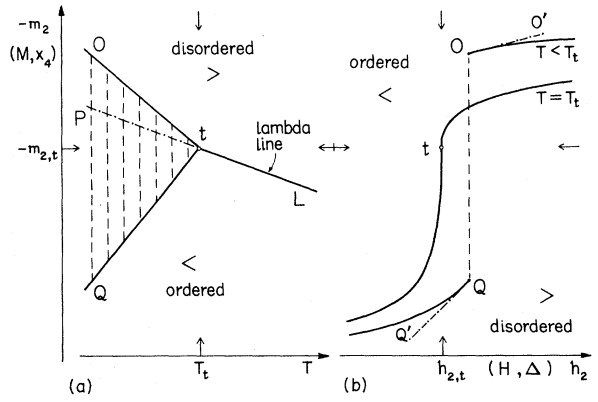

FIG. 1. (a) Tricritical phase diagram in the (m_2, T) plane. According to classical theory, the phase boundary $\overline{Ot}$ has the same slope as the λ line $\overline{tL}$. (b) Isotherms in the (m_2, h_2) plane. Classically, the tricritical isotherm for $h_2 > h_{2,t}$ has a finite slope at $h_2 = h_{2,t}$ and no singularity.

Now Fig. 1(a) depicts a prototypical tricritical phase diagram in the symmetry plane $h = h_3 = 0$; to within experimental resolution the phase boundaries, $\overline{Ot}$, $\overline{Qt}$, and $\overline{Lt}$, are asymptotically linear. On the other hand, the tricritical isotherm, in Fig. 1(b), verifies $|m_2 - m_{2,t}| \propto |h_2 - h_{2,t}|^{1/2}$ as $h_2 \to h_{2,t}$, or

$$(\partial m_2/\partial h_2)_T \approx B_{\gtrless}/|h_2 - h_{2,t}|^{1/2}, \text{ for } T = T_t, \quad (1)$$

where $<$ and $>$ refer to the ordered and disordered, regions respectively. Likewise, the tricritical "isochamp" may be described by

$$(\partial m_2/\partial h_2)_T \approx C_{\gtrless}/|t|^{1/2} \text{ for } h_2 = h_{2,t}. \quad (2)$$

Similarly, at the phase boundary $h_2 = h_{2,T}(T)$ below T_t, the slopes of $\overline{OO'}$ and $\overline{QQ'}$ in Fig. 1(b) obey

$$(\partial m_2/\partial h_2)_T \approx G_{\gtrless}/|t| \text{ for } h_2 = h_{2,T}, \ T < T_t. \quad (3)$$

All the exponents appearing here are those expected classically; we defer until the end the question of the logarithmic factors predicted by renormalization-group analysis.

We may now define the dimensionless ratios

$$\mathcal{Q}_1 = \overline{OP}/\overline{PQ}, \quad \mathcal{Q}_2 = B_>/B_<, \quad \mathcal{Q}_3 = C_>/C_<, \quad \mathcal{Q}_4 = G_>/G_<, \quad (4)$$

where P lies on the linear extension of the λ line as in Fig. 1(a). According to classical theory all these ratios vanish identically! This trivial universality does *not* extend to the $n \to \infty$ limit! Instead, in terms of the range parameter z, we find[5c]

$$\mathcal{Q}_2(z) = \mathcal{Q}_3(z) = z(1-z^2)^{-1/2} \equiv \tan\theta(z), \quad (5)$$

$$\mathcal{Q}_1(z) = \mathcal{Q}_4(z) = z(1-z^2)^{-1/2} \tan[\tfrac{1}{3}(\theta + \tfrac{1}{2}\pi)]. \quad (6)$$

For small z one has $\tan[\frac{1}{3}(\theta + \frac{1}{2}\pi)] \approx 3^{-1/2} + \frac{4}{9}z$. (Note that for $z > 1$ the tricritical point is replaced by a critical end point.)

The results (5) and (6) imply that one may predict all the ratios $\mathcal{Q}_i$ given any one of them! Indeed, from Giordano and Wolf's data[8] for the metamagnet dysprosium aluminum garnet (DyAlG) with $\vec{H} \| [110]$, one finds $\mathcal{Q}_1 = 0.145(10)$, which via (6) corresponds to $z = 0.210(12)$ (all uncertainties referring to the last decimal place). Through (5) this predicts $\mathcal{Q}_2^{\text{theor}} = 0.215(13)$ which compares well with the observed value $\mathcal{Q}_2 = 0.24(3)$. Likewise the fitted value,[8b] $\mathcal{Q}_4 = 0.125(25)$, satisfies the equality (6) within the precision available. Current data for $\vec{H} \| [111]$ in DyAlG and for other antiferromagnets do not allow us comparable tests. However, optical measurements[9] on $FeCl_2$ yield $\mathcal{Q}_1 \cong 0.24(4)$, corresponding to $z = 0.31(4)$; the significant departures from the DyAlG values demonstrate the nonuniversality.

From the thermodynamic and ultrasonic data of Ahlers and Greywall[10] and Meyer and collaborators[11] on helium three-four mixtures at vapor pressure, we may similarly estimate $\mathcal{Q}_1 = 0.086(15)$, $\mathcal{Q}_2 = 0.115(15)$, $\mathcal{Q}_3 = 0.125(15)$, and $\mathcal{Q}_4 = 0.09(3)$. Within the uncertainties $\mathcal{Q}_2$ and $\mathcal{Q}_3$ are equal, in accord with (5), and suggest $z = 0.120(15)$. The relation (6) then yields $\mathcal{Q}_1^{\text{theor}} = \mathcal{Q}_4^{\text{theor}} = 0.076(11)$. This is quite consistent with the estimates quoted. Furthermore, measurements by Watts and Webb,[12] who paid special attention to gravitational effects, yield $\mathcal{Q}_1 = 0.075(15)$, while light-scattering studies by Leiderer, Watts, and Webb[13] give $\mathcal{Q}_4 = 0.070(15)$, both in excellent agreement with the prediction! Data at high pressures might well reveal nonuniversality, and would, in any case, be valuable as a further check on the ratio relations.

Our analysis so far has been confined to strictly vanishing h_1 and h_3. For superfluids no more is observable, but the susceptibility $\chi = \partial m/\partial h_1$ is measurable in neutron-scattering experiments on antiferromagnets (at least for $h_1 \to 0$) and hence some related nonuniversal amplitude ratios could be studied. In fluid mixtures, however, nonzero h_1 and h_3 play a vital role.[2,6] The most dramatic phenomenon is the three-phase monohedron observed[14] in density space (m, m_2, m_3) at fixed $T < T_t$; see Fig. 2.

The shape of the monohedron is conveniently expressed using the scaling variables $w_j = \tilde{m}_j / A_j^0 |t|^{j/2}$, where

$$\tilde{m}_1 = m, \quad \tilde{m}_2 = m_2 - m_{2,c}(T), \quad \tilde{m}_3 = m_3 - btm, \quad (7)$$

in which b is a suitably chosen mixing parameter,[5c] $m_{2,c}(T)$ describes the locus $\overline{Pt}$ in Fig. 1(a), and the A_j^0 are the critical amplitudes for $E_+^0 = E_+(z=0)$. Classical theory[6,7] then gives the edge of the monohedron as $w_2 = w_1^2$, $w_3 = w_1^3$; this is reflected in the parabolic and near-cubic aspects of the projections illustrated in Figs. 3 and 2. Nonclassical deviations can be observed quantitatively in the ratios

$$\mathcal{R}_{0,j} = [\overline{O_+O}]_j / [\overline{E_+O}]_j, \quad \mathcal{R}_{c,j} = [\overline{C_+O}]_j / [\overline{E_+O}]_j, \quad (8)$$

where $[\ ]$ denotes the projection on the w_j axis. From a complete calculation[5c] to $O(z)$ of the

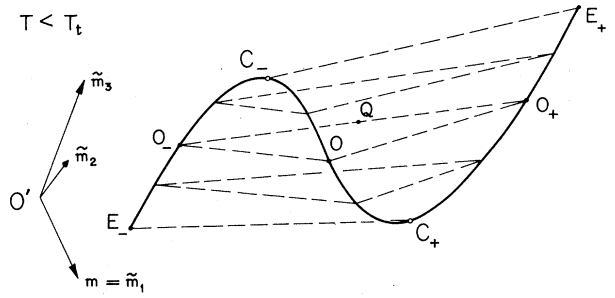

FIG. 2. General view of the three-phase monohedron in composition or density space. The vertices of each triangle of dashed lines represent the compositions of coexisting phases: C_+ and C_- are critical end points conjugate to E_- and E_+, respectively; Q is the midpoint of $\overline{C_+C_-}$ and O is the symmetry point or node (see Fig. 1); the $\tilde{m}_j$ label the scaling axes.

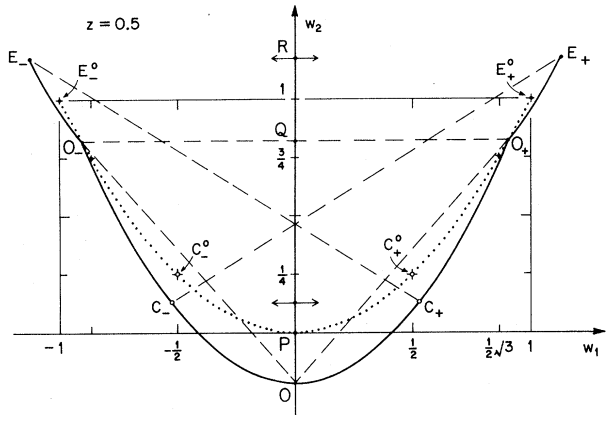

FIG. 3. View of the three-phase monohedron (solid curve) along the $w_3 \propto \tilde{m}_3$ axis plotted to first in z. The dotted parabola, $E_-{}^0O_-C_-{}^0PC_+{}^0O_+E_+{}^0$, represents the classical limit ($z=0$).

shape of the monohedron (for $n \to \infty$), we find

$$\mathcal{R}_{0,j} \approx (\tfrac{3}{4})^{j/2}[1 - e_{0,j}z],$$
$$\mathcal{R}_{c,j} \approx (\tfrac{1}{2})^{j}[1 - e_{c,j}z], \tag{9}$$

with $e_{0,1} = 65/243\sqrt{3} \simeq 0.154 \simeq 194/729\sqrt{3} = e_{c,1}$ and, in addition, $e_{0,2} \simeq e_{c,2} \simeq 0.02$, $e_{0,3} \simeq e_{c,3} \simeq 0.17$. Experimentally the ratios $\mathcal{R}_{0,1}$ and $\mathcal{R}_{c,1}$ are the most accessible since, as $T \to T_t$, they become equal to the ratios $\overline{O_+O_-}/\overline{E_+E_-}$ and $\overline{C_+C_-}/\overline{E_+E_-}$ of unnormalized composition differences; in particular, it is unnecessary to determine the scaling axes. If, as for magnets, $z = 0.1$ to 0.3, the predicted nonclassical deviations should be detectable by accurate measurements on multicomponent fluids even though current data[14] are not sufficiently precise.

In classical theory all the coexistence triangles become parallel asymptotically. This parallelism fails for $z > 0$ (and $n = \infty$) but the maximum residual angle, between $\overline{E_+C_-}$ and $\triangle O_+O_-O$, appears likely to be less than 1°. Other nonclassical features visible in Fig. 3, are the *kinks* in the edge of the monohedron at O_+ and O_-. These derive directly from the "soft," Goldstone modes which appear in the ordered phase on, but only on, the symmetry plane ($h = h_3 = 0$). We thus speculate that such kinks will be present for all $n \geq 2$. In normal fluids, however, $n = 1$ is appropriate and, although the edge might bend more or less sharply relative to classical theory, no kinks should occur at $O_\pm$. Conversely, in real multicomponent fluids, a marked flattening of the edge is observed[14] near the critical end points, $C_\pm$. This is believed to reflect the nonclassical wing critical exponent $1/\hat{\beta}(n=1) \simeq 3.2$, but, since $1/\hat{\beta}(n=\infty) = 2$, the effect is, unfortunately, absent from our calculations.[5]

Finally we ask why, in the light of the predicted logarithmic factors in $|t|$, $|h|$, etc.,[3] our calculations for $n = \infty$ should apply at all for $n < \infty$. A definitive answer must surely await detailed calculations for $n < \infty$. Nevertheless, noting that z corresponds to a *marginal variable* (which is irrelevant but dangerous[5] for $d > 3$), we speculate that a full analysis for finite n might, to a good approximation, replace z by an expression like $\tilde{z} = \{z_0 + z_1[\ln|t|/q)]^{\pi}\}$ with q and π functions of the scaled variables $h/|t|^{\Delta}$, etc., and $z_1(n) \to 0$ as $n \to \infty$. If q or z_0/z_1 were large, $\tilde{z}$ would be very slowly varying in practical tricritical experiments, so that observations would correlate well with a $\tilde{z} = \text{const}$ approximation.

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Diffraction of Photoelectrons Emitted from Core Levels of Te and Na Atoms Adsorbed on Ni(001)

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Azimuthal anisotropies in the photoemission from the Te 4*d* and Na 2*p* core levels have been measured for these atoms adsorbed in the $c(2\times2)$ configuration on Ni(001). The observed variations with photoelectron kinetic energy, polar angle of emission, and adsorbate species indicate that this is a very promising technique for surface-structure determination. Preliminary multiple-scattering calculations show encouraging agreement with experiments.

The availability of synchrotron radiation in the photon energy range $\hbar\omega > 30$ eV has led to proposals by Liebsch[1] and others[2,3] that measurements of the anisotropy of photoemission from the core levels of adsorbed atoms could be used to determine their positions relative to the surface. The wave function of the excited photoelectron is envisaged as a wave emanating from the atom of origin. This wave will scatter against substrate atoms, and the resulting electron interference pattern should be observable with an external detector. The theoretical prospects for a technique based on this effect appear quite good.[1,3-5] In contrast, the experimental situation has been less hopeful. Observations at low energy ($\hbar\omega = 24$ eV) of the emission from the 5*p* levels of Cs adsorbed on W(001) showed only weak anisotropies.[2] More recently, x-ray ($\hbar\omega = 1487$ eV) photoemission measurements of the 1*s* level of O adsorbed on Cu(001) showed somewhat larger anisotropies,[6] but such high-energy work appears to be restricted to grazing angles of emission presumably because of Debye-Waller effects and the weakness of all but forward scattering.[7]

Ideally, in such experiments, one would wish to tune $\hbar\omega$ so that the photoelectrons emerge with kinetic energies, E, in the range 30–200 eV appropriate to the conventional structural technique of low-energy electron diffraction (LEED). Synchrotron radiation is therefore essential. This would allow the extensive theoretical expertise accumulated in LEED studies to be transferred to the photoemission problem. It would also ensure strong backscattering amplitudes with only limited Debye-Waller degradation at room temperature.[7] Moreover, as in

