Nonclassical Equations of State for Critical and Tricritical Points

Jeffrey R. Fox[1,2]

We develop a method by which certain classical equations of state may be modified to produce nonclassical critical scaling behavior. We then apply this method to the classical free energy describing a tricritical point that was originally introduced by Griffiths. The phase behavior of the resulting nonclassical free energy is characterized by the competition between critical scaling and tricritical scaling already envisioned by previous authors.

1. INTRODUCTION

In an earlier paper[1] we examined the characteristic phase behavior associated with tricritical points (i.e., thermodynamic states in which three phases become simultaneously identical) in two classical fluid mixture models. The description of tricritical phenomena given by these classical formulations is self-consistent and in qualitative agreement with the very limited data presently available from experimental investigations of tricritical points in ternary and quaternary fluid mixtures.[3] We expect that the classically predicted phase diagrams are correct insofar as the basic topology of the various coexistence and critical manifolds is concerned. But classical equations of state are well known for their failure to correctly describe the merging of two phases at a critical point, and, since a tricritical point is intimately connected with critical points in these phase diagrams, we must seriously consider the

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[1] Department of Chemistry, Cornell University, Ithaca, New York.
[2] Present address: Department of Chemistry, Stanford University, Stanford, California.

[3] Footnotes 3–10 of Ref. 1 provide a comprehensive list of experimental investigations of tricritical points in fluid mixtures.

question of how and to what extent the classical picture of tricritical phenomena should be modified to take this failure into account.

A tricritical point is an invariant point for systems with four thermodynamic degrees of freedom. Figure 1 shows the connectivity of the triple point and critical surfaces near a tricritical point in a projection of the phase diagram in the space of four field[4] variables (e.g., the four-space of temperature and three independent chemical potentials). We see that the tricritical point lies on a surface of critical points and that every neighborhood of the tricritical point will contain part of this surface. Thus, even though the asymptotic variation (as a tricritical point is approached) of the thermodynamic quantities relevant to phase separation (in particular, the chemical compositions of phases in mutual equilibrium) are known from the calculations of the renormalization group theory to be classical[3] (at least insofar as their leading power law exponents are concerned), it would nevertheless be incorrect to suppose that the classical theory will become increasingly accurate when applied to ever smaller neighborhoods of such a point.

A more attractive hypothesis, originally introduced by Riedel[4] and examined by a number of authors,[5] may be stated as follows. We suppose that, as the state of a system approaches a point on the critical surface, the asymptotic variation of the relevant thermodynamic quantities will be accurately described by an appropriate generalization of the nonclassical scaling theory proposed by Widom[6] and known to be correct to within

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[4] We make the useful distinction, introduced by Griffiths and Wheeler,[2] between "field" variables, such as the temperature, pressure, and the component chemical potentials, which are always identical in two coexisting phases, and "density" variables, such as the mole fractions of particle number densities of the components, which are generally different in two coexisting phases.
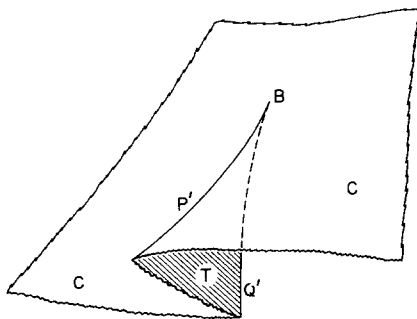

Fig. 1. A schematic representation of the triple point (T) and critical point (C) surfaces near a tricritical point (B) in a projection from the full four-dimensional field-space phase diagram. The two surfaces meet nontangentially at the critical end-point lines P' and Q'.

experimental error near ordinary critical points. But if the state of the system specifically approaches the tricritical point, these asymptotic variations will be of a form which satisfies classical tricritical scaling (i.e., the tricritical scaling behavior of the classical models). Thus, we expect that, as the state of a system varies along some trajectory in the space of the field variables (i.e., the space shown in Fig. 1), the resulting phase behavior will reflect a competition between the two different scaling influences, and that the relative dominance of one scaling influence or the other will be dependent upon the direction of this variation in the field space and upon the relative proximity of the critical surface and the tricritical point.

In the present paper we develop a method by which nonclassical critical scaling behavior may be incorporated directly into the formal structure of certain simple classical equations of state. In Section 2 we illustrate this method through its application to the case of a classical Landau expansion about a critical point, and in Section 3 we apply it to a Landau formulation describing a critical line. We have not been able to apply this method directly to the case of a tricritical point because of the additional complexity of the phase behavior near such a point. But, by making a number of additional assumptions which go beyond the critical scaling hypothesis upon which the method is based, we are finally able, in Section 4, to produce a nonclassical equation of state which describes a tricritical point. By obtaining such an equation of state, we are then able to investigate the resulting mechanism of the competition between nonclassical critical and classical tricritical scaling, and to indicate what discrepancies between the classical predictions and the behavior of real fluid mixtures may be expected.

2. NONCLASSICAL EQUATION OF STATE DESCRIBING A CRITICAL POINT

The procedure we introduce in this section for the incorporation of non-classical critical scaling into the structure of a classical equation of state has yet to be judged on any but the most pragmatic grounds. Though the scaling hypothesis upon which our procedure is based may be formally related to the homogeneity hypothesis of Widom,[6] we have not endeavored to make such a connection; we regard our method only as a mathematical technique designed to reproduce the nonclassical behavior of experimental systems and not as a theoretical statement about microscopic interactions and correlations which underlie this behavior.

We take the viewpoint that the gross implications of classical theory, such as the phase diagram in the field space, are qualitatively correct. But we now restructure the singular part of the classical free energy so that the next level of detail—the critical exponents associated with the variations of

the densities and higher derivatives of the free energy—becomes correct as well. And whereas we could in principle apply our method to a variety of phenomenological equations of state (e.g., that of van der Waals or the virial expansion to finite order), we apply it here to the Landau order-parameter expansion about a critical point because the general features of classical theory upon which our "reconstruction" is based are most readily apparent in this formulation.

In the Landau philosophy we suppose that the free energy of a system with two thermodynamic degrees of freedom may be approximated near a critical point by the form

$$F(a_1, a_2) = \min_\psi(a_1\psi + a_2\psi^2 + \psi^4) + B(a_1, a_2) \tag{1}$$

where the model field variables a_i are analytic functions of the real fields (e.g., temperature and pressure for a one-component fluid), $a_1 = a_2 = 0$ is the critical point, and $B(a_1, a_2)$ is an analytic background free energy. (The explicit relations between a_1, a_2, B, and the real fields will, of course, depend upon the particular system being modeled; but these relations are not important to our discussion here.)

We note that the polynomial in ψ may be reparametrized in the form

$$a_1\psi + a_2\psi^2 + \psi^4 = (\psi - c)^2[(\psi + c)^2 + R^2] - c^2(c^2 + R^2) \tag{2}$$

with the parameters c and R^2 defined by

$$a_1 = -2cR^2 \tag{3a}$$

$$a_2 = R^2 - 2c^2 \tag{3b}$$

and in this form we may trivially perform the indicated minimization over ψ, with the result that $F(a_1, a_2)$ may be expressed in a purely parametric form

$$F(a_1, a_2) = -c^2(c^2 + R^2) + B(a_1, a_2) \tag{4}$$

Now in terms of these parameters, the densities ρ_i conjugate to the fields a_i are

$$\rho_1 \equiv -\partial F/\partial a_1 = -c - B_1 \tag{5a}$$

$$\rho_2 \equiv -\partial F/\partial a_2 = -c^2 - B_2 \tag{5b}$$

with $B_i \equiv \partial B/\partial a_i$ (and thus analytic in the a_i).

When the values of a_1 and a_2 are such that the polynomial in Eq. (2) has two equal minima [i.e., such that two different sets of values of c and R^2 are consistent with Eq. (3)], then the point (a_1, a_2) is a point of two-phase coexistence in the a_i field space, and the two corresponding points in the ρ_i density space are the compositions of the two phases in mutual equilibrium. The phase diagrams of this model may thus be trivially determined; the two-

phase region is characterized by $a_1 = 0$, $a_2 \leqslant 0$ (or, parametrically, $R^2 = 0$), and in this region (i.e., on this coexistence curve in the field space) the densities are (plus and minus signs indicating the two equilibrium phases)

$$\rho_1(\pm) = \pm(-a_2/2)^{1/2} - B_1 \tag{6a}$$

$$\rho_2(\pm) = \tfrac{1}{2}a_2 - B_2 \tag{6b}$$

The field-space and density-space phase diagrams of this model are shown in Fig. 2. In the a_i field space (Fig. 2a), the negative a_2 axis is the coexistence curve, and it terminates in a critical point at the origin. The ρ_i density-space phase diagram is characterized by a binodal curve (the "classical" curve indicated in the figure) composed of the end points of the lines joining equilibrium phases.

The results of experimental investigations near critical points may be expressed in this language by the asymptotic relations

$$\rho_1 + B_1 \sim (-a_2)^\beta \tag{7a}$$

$$\rho_2 + B_2 \sim (-a_2)^{1-\alpha} \tag{7b}$$

with the critical exponent values $\beta \approx 0.35$ and $\alpha \approx 0.1$ for pure fluids.[7] That is, we expect that if we make an analogy between the field-space phase diagram, Fig. 2a, and that of a real fluid in the near-critical region, we would expect the corresponding binodal curve to be consistent with the asymptotic relation

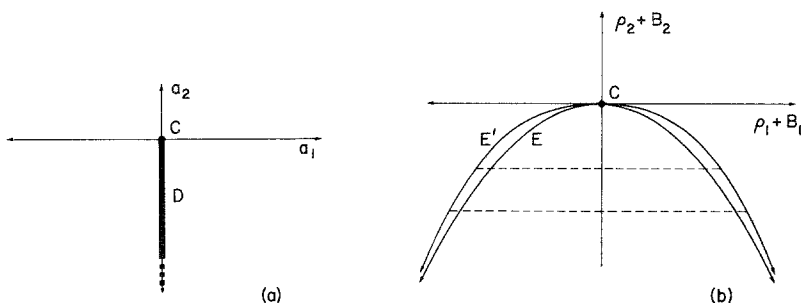$$(\rho_2 + B_2) \sim |\rho_1 + B_1|^{(1-\alpha)/\beta}$$

Fig. 2. (a) Field-space phase diagram of the classical Landau expansion about a critical point [Eq. (1)] and, identically, the field-space phase diagram of the corresponding nonclassical system [Eq. (18)]. The coexistence curve D terminates in a critical point C. (b) Density-space phase diagram of the classical system [Eq. (1)] and the corresponding nonclassical system [Eq. (18)]. E is the binodal curve of the classical system and E′ is that of the nonclassical system. The dashed lines are typical tie-lines joining phases in mutual equilibrium.

and thus have significantly less curvature at the critical point than the classically predicted parabola. (The difference between these curves is again shown in Fig. 2b.)

So we see that in order to produce the density relations characteristic of experimental systems, we must somehow change the way the singular part of the free energy

$$F_s(a_1, a_2) = \min_{\psi}(a_1\psi + a_2\psi^2 + \psi^4) = -c^2(c^2 + R^2) \tag{8}$$

varies or "scales" with the fields a_j as the critical point $a_1 = a_2 = 0$ is approached. We may express the classical scaling by the relation

$$F_s(a_1, a_2) = \lambda^{-4}F_s(\lambda^3 a_1, \lambda^2 a_2) \tag{9}$$

(where λ is any positive parameter), or, upon differentiation,

$$\rho_{is}(a_1, a_2) \equiv -\partial F_s/\partial a_i = \lambda^{-i}\rho_{is}(\lambda^3 a_1, \lambda^2 a_2) \tag{10}$$

(i.e., ρ_{is} is the contribution to ρ_i from F_s).

Now suppose we could replace $F_s(a_1, a_2)$ with a new singular function F_s' with the scaling property

$$F_s'(a_1, a_2) = \lambda^{-4}F_s'(\lambda^{3+\phi}a_1, \lambda^{2+\theta}a_2) \tag{11}$$

i.e., a new scaling form which differs from the classical form by the "small" exponents θ and ϕ. We would then have new density relations with the scaling

$$\rho_{1s}'(a_1, a_2) = \lambda^{\phi-1}\rho_{1s}'(\lambda^{3+\phi}a_1, \lambda^{2+\theta}a_2) \tag{12a}$$

$$\rho_{2s}'(a_1, a_2) = \lambda^{\theta-2}\rho_{2s}'(\lambda^{3+\phi}a_1, \lambda^{2+\theta}a_2) \tag{12b}$$

and, if F_s' is constructed such that it generates the same phase diagram as F_s in the field space, the densities in the two-phase region will obey

$$\rho_{1s}'(0, a_2) = |a_2|^{(1-\phi)/(2+\theta)}\rho_{1s}'(0, -1) \tag{13a}$$

$$\rho_{2s}'(0, a_2) = |a_2|^{(2-\theta)/(2+\theta)}\rho_{2s}'(0, -1) \tag{13b}$$

i.e., $\rho_{1s}' \sim (-a_2)^\beta$ and $\rho_{2s}' \sim (-a_2)^{1-\alpha}$, the desired behavior, with the identifications $\beta = (1 - \phi)/(2 + \theta)$ and $1 - \alpha = (2 - \theta)/(2 + \theta)$.

We describe the task of constructing a function F_s' which has the indicated properties as the reconstruction or "rescaling" of F_s (or more generally as the rescaling of the classical free energy F). Now we could equally well have described the "rescaling" in terms of the parameters c and R of the parametric representation of $F(a_1, a_2)$. For example, we could introduce the function F_s' parametrically:

$$F_s'(a_1, a_2) = -c^2(c^2 + R^2) \tag{14}$$

but now with

$$a_1 = -2cR^2[g(c, R)]^\phi \tag{15a}$$

and

$$a_2 = (R^2 - 2c^2)[g(c, R)]^\theta \tag{15b}$$

where $g(c, R)$ is a positive-valued scaling function with the scaling property $g(c, R) = \lambda^{-1}g(\lambda c, \lambda R)$. This construction implies that

$$a_1(c, R) = \lambda^{-3-\phi}a_1(\lambda c, \lambda R) \tag{16a}$$

and

$$a_2(c, R) = \lambda^{-2-\theta}a_2(\lambda c, \lambda R) \tag{16b}$$

and thus

$$F_s'(a_1, a_2) = \lambda^{-4}F_s'(\lambda^{3+\phi}a_1, \lambda^{2+\theta}a_2) \tag{17}$$

i.e., F_s' has the desired scaling form. We have reduced the problem of rescaling $F(a_1, a_2)$, then, to the problem of finding an appropriate positive homogeneous function $g(c, R)$. It can be easily shown that the field-space phase diagrams of F and F' are identical if $g(c, R)$ is chosen such that it is an increasing function of the radial distance from the origin of the c, R plane on any straight line through that origin. Note that the scaling properties of g imply that $g(0, 0) = 0$.

One possible choice for $g(c, R)$ is the radial distance itself, i.e., $g(c, R) = (k_1R^2 + k_2c^2)^{1/2}$, where k_1 and k_2 are positive coefficients (arbitrary metrics of the parameter space). But more generally any of the family of functions $g(c, R) = (k_1R^{2n} + k_2c^{2n})^{1/2n}$ with n a positive integer would also apparently be acceptable. Another example is $g(c, R) = [(-2cR^2)^4 + (R^2 - 2c^2)^6]^{1/12}$ which, despite its complexity, does in fact simplify the calculation of the resulting densities. Using this last choice of $g(c, R)$, we may rewrite the rescaled free energy in the form

$$F'(a_1, a_2) = \min_\psi(b_1\psi + b_2\psi^2 + \psi^4) + B(a_1, a_2) \tag{18}$$

with the variables b_1 and b_2 defined by

$$a_1 = b_1(b_1^4 + b_2^6)^{\phi/12} \tag{19a}$$

$$a_2 = b_2(b_1^4 + b_2^6)^{\theta/12} \tag{19b}$$

In this particular case, the densities on the coexistence curve $(a_1 = 0, a_2 \leqslant 0)$ are

$$\rho_1'(\pm) = \pm 2^{-1/2}(-a_2)^\beta - B_1 \tag{20a}$$

and

$$\rho_2'(\pm) = -[1/(2 + \theta)](-a_2)^{1-\alpha} - B_2 \tag{20b}$$

with $\beta = (1 - \phi)/(2 + \theta)$ and $1 - \alpha = (2 - \theta)/(2 + \theta)$ as before (note that

the classical results are immediately recovered by setting θ and ϕ equal to zero). [Similar calculations using the other choices of $g(c, R)$ mentioned above differ from these results only in the coefficients of the singular terms and then only by powers or factors of ϕ and θ.] The resulting binodal curve is also shown in Fig. 2b.

So, despite the fact that our procedure is not very well defined by this one example, we have produced a new free energy formulation which, when "fitted" by setting θ and ϕ equal to their experimental values, will have the desired characteristics. We will not here calculate any further thermo-dynamic quantities, but the reader may be assured by the fact that F_s' is a scaling function that the exponents associated with these quantities will be those predicted by the so-called "scaling relations," which are known to be correct to within experimental error for fluid systems (Ref. 8, Table 3.4). We note that this new equation of state is very similar in many respects to that of Schofield,[8] and we expect that it has many of the same attributes.

3. NONCLASSICAL EQUATION OF STATE DESCRIBING A CRITICAL LINE

In order to consider the application of the rescaling idea to the case of a coexistence surface terminating in a critical line, we must first choose a classical system with three degrees of freedom which shows the appropriate behavior. As in the previous case, in principle any of a number of phenomeno-logical equations of state might be used, but for simplicity we choose a system of the Landau type; in this case, an order-parameter expansion about one point a critical line. The free energy in question is

$$F(a_1, a_2, a_3) = \min_{\psi}(a_1\psi + a_2\psi^2 + a_3\psi^3 + \psi^4) + B(a_1, a_2, a_3) \quad (21)$$

where again the model fields a_j are analytic functions of the real fields and $B(a_1, a_2, a_3)$ is an analytic background.

We note that we may also write this free energy in a parametric form, i.e.,

$$F(a_1, a_2, a_3) = -c_1{}^2(c_2{}^2 + R^2) + B(a_1, a_2, a_3) \quad (22)$$

with the parameters c_1, c_2, and R^2 defined by

$$a_1 = -2c_1R^2 - 2c_1c_2(c_1 + c_2) \quad (23a)$$

$$a_2 = R^2 + c_1{}^2 + c_2{}^2 + 4c_1c_2 \quad (23b)$$

$$a_3 = -2(c_1 + c_2) \quad (23c)$$

and in terms of these parameters, the conjugate densities are

$$\rho_i = -c_1{}^i - B_i(a_1, a_2, a_3) \quad (24)$$

But we may also greatly simplify the form of $F(a_1, a_2, a_3)$ by a change of variable $\eta \equiv \psi - a_3/4$; i.e.,

$$F(a_1, a_2, a_3) = \min_{\eta}(b_1\eta + b_2\eta^2 + \eta^4) + E + B \qquad (25)$$

with

$$b_1 = a_1 - \tfrac{1}{2}a_2a_3 + \tfrac{1}{8}a_3{}^3 \qquad (26a)$$

$$b_2 = a_2 - \tfrac{3}{8}a_3{}^2 \qquad (26b)$$

$$E = -\tfrac{1}{4}a_1a_3 + a_2(a_3/4)^2 - 3(a_3/4)^4 \qquad (27)$$

Since $E(a_1, a_2, a_3)$ is analytic in the fields, it may be treated as another background, and we see that the singular part of F is of the same form we treated in the previous section. But here the conditions for coexisting phases ($b_1 = 0, b_2 \leqslant 0$) describe a surface in the a_j field space, and the critical conditions $b_1 = b_2 = 0$ describe a critical line bounding that surface. The phase diagram in the a_j field space is shown schematically in Fig. 3.

Now in the parametric form, we have

$$F = -\tfrac{1}{4}(c_1 - c_2)^2[\tfrac{1}{4}(c_1 - c_2)^2 + R^2] + E + B \qquad (28)$$

with $(c_1 - c_2)$ and R^2 defined by

$$b_1 = a_1 - \tfrac{1}{2}a_2a_3 + \tfrac{1}{8}a_3{}^2 = -(c_1 - c_2)R^2 \qquad (29a)$$

$$b_2 = a_2 - \tfrac{3}{8}a_3{}^2 = R^2 - \tfrac{1}{2}(c_1 - c_2)^2 \qquad (29b)$$

We now replace F_s with $F_s{}'$ by rescaling the scaling fields b_i; i.e., the rescaled free energy is

$$F'(a_1, a_2, a_3) = -\tfrac{1}{4}(c_1 - c_2)^2[\tfrac{1}{4}(c_1 - c_2)^2 + R^2] + E + B \qquad (30)$$

but with the new definitions for $(c_1 - c_2)$ and R^2,

$$b_1 = a_1 - \tfrac{1}{2}a_1a_3 + \tfrac{1}{8}a_3{}^2 = -(c_1 - c_2)R^2[g(c_1 - c_2, R)]^\phi \qquad (31a)$$

$$b_2 = a_2 - \tfrac{3}{8}a_3{}^2 = [R^2 - \tfrac{1}{2}(c_1 - c_2)^2][g(c_1 - c_2, R)]^\theta \qquad (31b)$$

with g again chosen such that it fulfills the conditions outlined in the previous section. To illustrate the results of this formulation, we choose

$$g = \{[-(c_1 - c_2)R^2]^4 + [R^2 - \tfrac{1}{2}(c_1 - c_2)^2]^6\}^{1/12} \qquad (32)$$

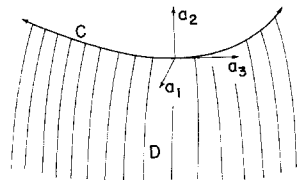a form completely analogous to that we used before.

Fig. 3. Projection of the a_i field-space phase diagram that arises from the Landau order-parameter expansion about a point on a critical line [Eq. (21)] [or from the corresponding nonclassical system, Eq. (30)]. The coexistence surface (D) terminates in a critical line (C) passing through the origin.

The resulting densities conjugate to the a_j are, on the coexistence surface,

$$\rho_1'(\pm) = \pm 2^{-1/2}(-b_2)^\beta - E_1 - B_1 \tag{33a}$$

$$\rho_2'(\pm) = \mp 2^{-3/2}a_3(-b_2)^\beta - \frac{1}{2+\theta}(-b_2)^{1-\alpha} - E_2 - B_2 \tag{33b}$$

$$\rho_3'(\pm) = \pm 3(2)^{-9/2}a_3^2(-b_2)^\beta + \frac{3}{4}\frac{a_3}{2+\theta}(-b_2)^{1-\alpha}$$
$$\pm 2^{-3/2}(-b_2)^{1+\beta} - E_3 - B_3 \tag{33c}$$

The field-space phase diagram for this system is identical to that of the classical system (Fig. 3). The resulting phase diagram in the space of the density variables will depend explicitly upon the background term $B(a_1, a_2, a_3)$, but it is obvious that the binodal surface described parametrically by the density relations above will be nonanalytic (for appropriate nonclassical values of β and α) at the critical line $b_2 = 0$. In order to appreciate the nonanalytic curvature of this surface, it is convenient first to consider the density-space phase behavior which is developed as the field space point representing the state of the system moves along the coexistence surface and approaches some particular point of the critical line. Every such trajectory on the coexistence surface will develop the same qualitative behavior (provided it approaches the critical line nontangentially) since, as Griffiths and Wheeler[2] have pointed out, no particular critical point on the line or angle of trajectory incidence is any way thermodynamically special. But the interpretation of this behavior is relatively simple, because of our particular choice of parametrization, on the trajectory defined by $a_1 = a_3 = 0$. The three-dimensional binodal space curve (in the density space) which corresponds to this field space trajectory has the asymptotic form [about the critical point $\rho_i' = \rho_{ic}'$, i.e., $\rho_{ic}' = -B_i(0, 0, 0)$ is the critical value of ρ_i']

$$(\rho_2' + B_2) \sim -|\rho_1' + B_1|^{(1-\alpha)/\beta} \tag{34a}$$

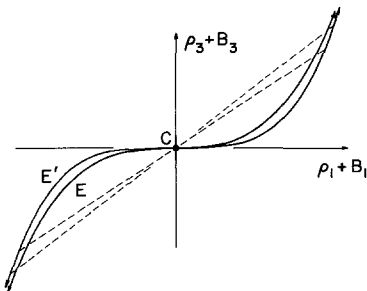$$(\rho_3' + B_3) \sim |\rho_1' + B_1|^{(1+\beta)/\beta} \, \mathrm{sgn}(\rho_1' + B_1) \tag{34b}$$

Fig. 4. The binodal space curves generated by the $a_1 = a_3 = 0$ trajectory projected onto the $\rho_2 = 0$ plane of the density space. E is the space curve of the classical system [Eq. (21)], and E' is that of the corresponding nonclassical system [Eq. (30)]. The dashed lines are tielines and C is the critical point. A projection of these curves onto the $\rho_3 = 0$ plane, instead, would be identical in every respect to Fig. 2b.

Perspectives of this space curve are shown and contrasted with the classical binodal curve in Fig. 4. Along any other trajectory the curve itself would be qualitatively similar, but the ρ_i axes would no longer have any special orientation with respect to the curve. We note that the curvature of this binodal space curve at the critical point is significantly less than that of the classical curve, and thus the binodal surface, which may be viewed as a smoothly varying, close-packed series of such curves, will be flattened about the critical line in comparison to the classical binodal surface.

This completes our discussion of this system, but before we turn to the case of near-tricritical nonclassical phase behavior, it is appropriate to summarize the mechanics of the rescaling technique insofar as they have been illustrated by these simple cases. In both cases we isolated out a singular part of the free energy with the form $F_s = -c^2(c^2 + R^2)$, where $R^2 = 0$ was a parametric description of the coexistence manifold and $R^2 = 0$, $c = 0$ the critical locus. We then redefined the relationship between the scaling fields and the parameters c and R^2 by changing the parametric representations of those fields, $-2cR^2$ and $R^2 - 2c^2$, to the "nonclassical" representations $-2cR^2g^\phi$ and $(R^2 - 2c^2)g^\theta$ with $g(c, R)$ an appropriate homogeneous function.

4. NONCLASSICAL EQUATION OF STATE DESCRIBING A TRICRITICAL POINT

We consider now the problem of constructing an equation of state which scales nonclassically as a critical manifold is approached, but which reproduces the classical tricritical scaling as a tricritical point is approached.

Again, we take a Landau formulation—the order-parameter expansion about a tricritical point originally investigated by Griffiths[9] and examined by us in the previous paper[1]—as our "base" classical system, since we presume that it approximates arbitrarily well the near-tricritical phase behavior of any other classical system. This free energy has the form

$$F(a_1, a_2, a_3, a_4) = \min_\psi(a_1\psi + a_2\psi^2 + a_3\psi^3 + a_4\psi^4 + \psi^6)$$
$$+ B(a_1, a_2, a_3, a_4) \tag{35}$$

where again the model fields a_i are analytic functions of the real fields, and $B(a_1, a_2, a_3, a_4)$ is an analytic background.

We may rewrite the singular part of this free energy in the form

$$F_s = \min_\psi\{(\psi - c_1)^2[(\psi - c_2)^2 + R_1^2][(\psi - c_3)^2 + R_2^2]\}$$
$$- c_1^2(c_2^2 + R_1^2)(c_3^2 + R_2^2) \tag{36}$$

with the parameters c_i, $R_j{}^2$ defined by

$$0 = c_1 + c_2 + c_3 \tag{37a}$$

$$a_1 = 2(c_2 + c_3)R_1{}^2R_2{}^2 - 2c_2c_3(c_2 + c_3)(R_1{}^2 + R_2{}^2 + c_2{}^2 + c_3{}^2 + c_2c_3) \tag{37b}$$

$$a_2 = (c_2{}^2 + c_3{}^2 + c_2c_3)^2 + (c_2{}^2 - 2c_2c_3 - 2c_3{}^2)R_1{}^2$$
$$+ (c_3{}^2 - 2c_2c_3 - 2c_2{}^2)R_2{}^2 + R_1{}^2R_2{}^2 \tag{37c}$$

$$a_3 = 2c_2c_3(c_2 + c_3) + 2c_2R_1{}^2 + 2c_3R_2{}^2 \tag{37d}$$

$$a_4 = R_1{}^2 + R_2{}^2 - 2(c_2{}^2 + c_3{}^2 + c_2c_3) \tag{37e}$$

and thus, since the minimization may now be simply performed, we have the parametric form

$$F = -c_1{}^2(c_2{}^2 + R_1{}^2)(c_3{}^2 + R_2{}^2) + B \tag{38}$$

Now the critical manifolds are defined parametrically by the relations $c_1 = c_2$, $R_1 = 0$ or the relations $c_1 = c_3$, $R_2 = 0$ (i.e., these are loci of points where two equal minima of the polynomial in ψ merge). Thus, we might expect that we must first separate out from F_s terms of the form

$$-\tfrac{1}{4}(c_1 - c_2)^2[\tfrac{1}{4}(c_1 - c_2)^2 + R_1{}^2] \quad \text{and} \quad -\tfrac{1}{4}(c_1 - c_3)^2[\tfrac{1}{4}(c_1 - c_3)^2 + R_2{}^2]$$

in analogy with the manipulation of the parametric form $-c_1{}^2(c_2{}^2 + R^2)$ into the form $-\tfrac{1}{4}(c_1 - c_2)^2[\tfrac{1}{4}(c_1 - c_2)^2 + R^2]$ we performed in the previous section using a change of variable. Unfortunately, we have not found any such simple manipulation for this case. Nevertheless, we may guess the form the rescaled equation might take, based on our experience with the previous examples. We propose the form

$$F' = F + h_1\{\tfrac{1}{4}(c_1 - c_2)^2[\tfrac{1}{4}(c_1 - c_2)^2 + R_1{}^2] - \tfrac{1}{4}(s_1 - s_2)^2[\tfrac{1}{4}(s_1 - s_2)^2 + Q_1{}^2]\}$$
$$+ h_2\{\tfrac{1}{4}(c_1 - c_3)^2[\tfrac{1}{4}(c_1 - c_3)^2 + R_2{}^2] - \tfrac{1}{4}(s_1 - s_3)^2[\tfrac{1}{4}(s_1 - s_3)^2 + Q_2{}^2]\} \tag{39}$$

where F is the classical free energy above, and h_1 and h_2 are as yet unknown functions but must be purely quadratic in the c_i, R_j parameters since F_s (and thus $F_s{}'$) must be sixth order overall. The s_i, Q_j are the "rescaled" parameters (with scaling yet to be defined); that is, the classical terms in c_i, R_j are subtracted from the classical free energy and replaced with s_i, Q_j terms of the same form. We imagine that the mechanical aspects of the rescaling of these variables would produce definitions of the form

$$-(s_1 - s_2)Q_1{}^2g_1{}^\phi = -(c_1 - c_2)R_1{}^2g_0{}^\phi \tag{40a}$$

$$[Q_1{}^2 - \tfrac{1}{2}(s_1 - s_2)^2]g_1{}^\theta = [R_1{}^2 - \tfrac{1}{2}(c_1 - c_2)^2]g_0{}^\theta \tag{40b}$$

$$-(s_1 - s_3)Q_2{}^2g_2{}^\phi = -(c_1 - c_3)R_2{}^2g_0{}^\phi \tag{40c}$$

$$[Q_2{}^2 - \tfrac{1}{2}(s_1 - s_3)^2]g_2{}^\theta = [R_2{}^2 - \tfrac{1}{2}(c_1 - c_3)^2]g_0{}^\theta \tag{40d}$$

where $g_1 = g_1(s_1 - s_2, Q_1)$ and $g_2 = g_2(s_1 - s_3, Q_2)$ are scaling functions of the "distance" in the parameter space to the critical loci $s_1 = s_2$, $Q_1 = 0$ (i.e., $c_1 = c_2$, $R_1 = 0$) and $s_1 = s_3$, $Q_2 = 0$ (i.e., $c_1 = c_3$, $R_2 = 0$), respectively; and where $g_0 = g_0(c_1 - c_2, c_1 - c_3, R_1, R_2)$ is a scaling function of the "distance" to the tricritical point $(c_1 = c_2, c_1 = c_3, R_1 = 0, R_2 = 0)$; i.e., where g_0 has the scaling property

$$g_0[(c_1 - c_2), (c_1 - c_3), R_1, R_2] = \lambda^{-1} g_0[\lambda(c_1 - c_2), \lambda(c_1 - c_3), \lambda R_1, \lambda R_2] \quad (41)$$

The point of these complexities is that in this formulation the parameters s_i, Q_j always scale with their c_i, R_j counterparts as the tricritical point is approached; thus the classical tricritical scaling, expressed by the relation

$$F_s(a_1, a_2, a_3, a_4) = \lambda^{-6} F_s(\lambda^5 a_1, \lambda^4 a_2, \lambda^3 a_3, \lambda^2 a_4) \quad (42)$$

is preserved in F_s' in spite of the rescaling. But as a critical manifold is approached, the appropriate set of s_i, Q_j parameters—for example, $s_1 - s_2$ and Q_1 as c_1 approaches c_2 and R_1 approaches zero—scales nonclassically with the "scaling fields" $-(c_1 - c_2)R_1^2$ and $R_1^2 - \frac{1}{2}(c_1 - c_2)^2$ because g_1 will vanish, while g_0 must remain asymptotically constant.

We may expect then that, if we can choose some appropriate specific form for the functions h_i and g_j, the resulting free energy will have the mixture of classical and nonclassical scaling we hypothesized in the first section. But choosing these remaining undefined functions such that the overall thermodynamic stability of the system is maintained has proven very difficult. In order to proceed, we have been forced to choose h_1, h_2, g_0 such that (besides preserving the exchange symmetry $c_2 \leftrightarrow c_3$, $R_1 \leftrightarrow R_2$) a number of "critical matching conditions" are satisfied. The first of these matching conditions is that as g_1 approaches zero (i.e., as the $R_1 = 0$, $c_1 = c_2$ critical manifold is approached), g_0 must rapidly converge to g_2, and similarly, as g_2 approaches zero, g_0 must rapidly converge to g_1. The effect of this behavior is that as one critical manifold is approached, the s_i, Q_j associated with the other critical manifold rapidly converge to their counterpart classical parameters and thus cancel out in the free energy formulation above. The second matching condition stems from the fact that there is a critical condition not considered above, namely $c_2 = c_3$ with $R_1 = R_2 = 0$. This critical condition does not describe a critical point in the density space; rather, it describes the noncritical phase in equilibrium with a critical phase at a critical end point. The resulting matching condition is that, on this manifold, we must have $g_0 = g_1 = g_2$ and $h_1 = h_2 = 0$ (but the h_i must not vanish elsewhere).

We do not know at this point whether these conditions are fully sufficient for the stability of this free energy formulation. But by satisfying them in the most direct way we have been able to produce stable and apparently

satisfactory equations of state. We first choose the functions h_i, since this choice is not dependent upon the details of the g_j functions. We imagine $h_1 = h_2$ with the general form

$$h_1 = h_2 = D[\tfrac{1}{4}(c_2 - c_3)^2 + R_1{}^2 + R_1{}^2] \tag{43}$$

where D is a positive constant of order unity. Now the functions g_1 and g_2 could have any form consistent with the restrictions indicated in previous sections, but they must both have the same form, since in essence they both describe the same manifold in the density space. For example, using one of the general forms for g indicated in Section 2, we may choose

$$g_1(s_1 - s_2, Q_1) = [k_1 Q_1^{4n} + k_2(s_1 - s_2)^{4n}]^{1/4n} \tag{44}$$

$$g_2(s_1 - s_3, Q_2) = [k_1 Q_2^{4n} + k_2(s_1 - s_3)^{4n}]^{1/4n} \tag{45}$$

(where we have changed $2n$ to $4n$ to facilitate the resulting definition for g_0). The matching conditions on g_0 may be relatively easily satisfied; for example,

$$
\begin{aligned}
g_0 = [&k_1 R_1^{4n} + k_1 R_2^{4n} + k_2(c_1 - c_2)^{4n} + k_2(c_1 - c_3)^{4n} \\
&- k_2(c_1 - c_2)^{2n}(c_1 - c_3)^{2n}]^{1/4n}
\end{aligned}
\tag{46}
$$

is consistent with this choice of g_1 and g_2. There are, of course, innumerable other possibilities for these functions g_j, some of which we will discuss later, but they differ only in details unrelated to the scaling properties, which are our primary interest here.

In view of the algebraic complexity of this formulation, it would be very difficult to survey all of the important behavior of this model, and we have not, in fact, done so, except through numerical calculation on various manifolds of interest. Nevertheless, we may make some useful generalizations about the competition between the classical and nonclassical influences. We note first that the field-space phase diagram of the nonclassical model is identical to that of the classical system. But as the state of the system approaches the critical manifold (along, say, the coexistence manifold), the nonclassical densities have the asymptotic form

$$
\begin{aligned}
\rho_i{}'(\pm) = \rho_i(\pm) &\pm q_i d_t^{(i-1)/2}(r_i d_c{}^\beta d_t^{1/2-\beta} - d_c^{1/2}) - w_i d_t^{(i-2)/2}(v_i d_c^{1-\alpha} d_t^\alpha - d_c) \\
&+ \text{higher order terms in } d_c
\end{aligned}
\tag{47}
$$

where plus and minus indicate the two merging phases, ρ_i is the classical value of the density i, the coefficients q_i, r_i, w_i, and v_i are constants depending upon the trajectory of approach (q_i and w_i may be zero on trajectories with special symmetries), and d_c and d_t are scaling functions proportional to the "distances" in the field space to the critical point in question and to the tricritical point, respectively. One can see that the length of the associated tie-lines joining the two phases vanishes as the β power of the difference

between the fields a_j and their critical values a_{jc}, since $(a_j - a_{jc}) \sim d_c$, and d_t is asymptotically constant. [But note that the terms with nonclassical exponents in Eq. (47) are always followed by terms with the complimentary classical exponents.] On the other hand, as the tricritical point is approached, $d_c \sim d_t$, and thus on such trajectories all of the nonclassical exponents "cancel out," leaving only the classical scaling $\rho_i' \sim \rho_i \sim d_t^i$. We note also that on the critical manifold ($d_c = 0$), the critical densities of the rescaled system are exactly equal to the classical critical densities.

The coefficients r_i and v_i are very nearly equal to unity, and thus when the state of the system is far from critical (i.e., when d_c is near d_t), the deviation of the densities ρ_i' from their classical values becomes very insignificant. Thus, it is only in the near-critical region of the field space characterized by $(d_c/d_t)^\beta \ll 1$ that we see significant qualitative and quantitative differences between the classical and nonclassical models, and even then qualitative differences will show up only along trajectories on which d_c varies significantly. In particular, the phase behavior along a trajectory which is very near and parallel to the critical surface, or along a trajectory on the surface, will be almost or exactly identical in the two models.

Before concluding our discussion of the scaling properties, it is appropriate to consider the resulting nonclassical geometry of the isothermal three-phase region investigated classically in the previous paper.[1] We associated the field a_4 with the temperature $(T - T_t)$, with T_t the tricritical temperature, and in an iso-a_4 (i.e., isothermal) section of the density space, the three-phase region was described as a stack of parallel triangles lying between two end-point tie-lines (degenerate triangles) as in Fig. 5. Classically, the vertices of the triangles define a single, smooth, analytic curve which we called the three-phase equilibrium curve. Since that curve passes through two different critical points (P' and Q' in the figure), we must expect that
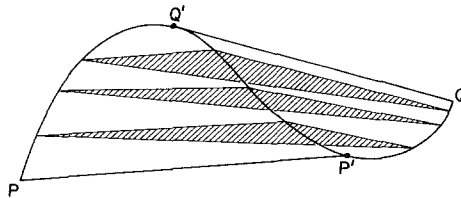

Fig. 5. A schematic drawing showing the topology of the three-phase region in an isothermal composition space. The region is a three-dimensional volume spanned by an infinite series of triangles (three of which are indicated in the figure) extending between the degenerate triangles $\overline{PP'}$ and $\overline{QQ'}$. The points in the interior of each triangle represent mixtures unstable with respect to separation into the three equilibrium phases whose compositions lie at the vertices of the triangles. P' and Q' are critical phases, each in equilibrium with a noncritical phase (P and Q, respectively).
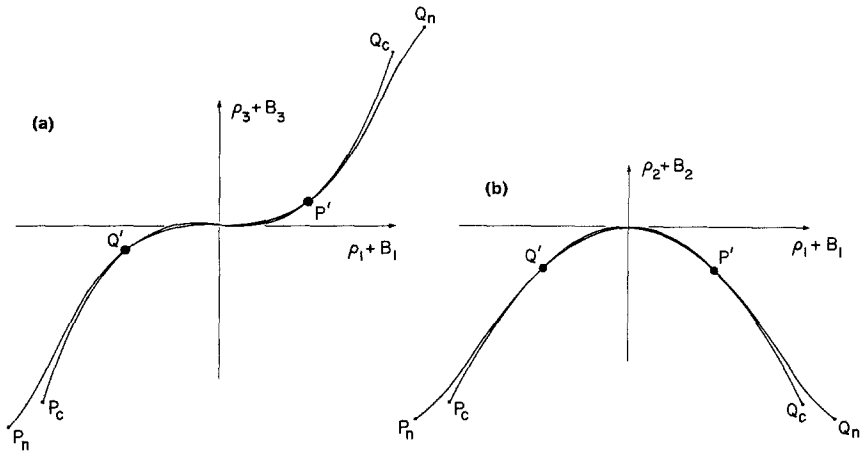
Fig. 6. (a) Comparison of the classical ($Q_c P'Q'P_c$) and nonclassical ($Q_n P'Q'P_n$) three-phase equilibrium curves projected into the $\rho_2 = 0$ plane of the density space with the parameter values $\alpha = 0.1$, $\beta = 0.35$, $n = 2$, $k_1 = k_2 = 1.0$, $a_4 = -1.5$, and $D = 1.5$ (D has been chosen greater than unity to visually emphasize the discrepancies between the curves). The classical curve is another perspective of the curve $QP'Q'P$ shown in Fig. 5. The triangles joining equilibrium phases are not shown, for the sake of clarity, but in the classical case they are mutually parallel (and perpendicular to the plane of the projection), and in the nonclassical case they are almost, but not exactly, parallel. (b) The same curves as in (a), but here projected into the $\rho_3 = 0$ plane.

in the present case, there will be a nonclassical flattening near these critical points and that the curve will be nonanalytic there but remain analytic elsewhere. In fact, the shape of this curve near one of the critical points is asymptotically the same as the shape—which we studied in the previous section—of the nonclassical binodal curve at a critical point. In particular, the parabolic aspect of the classical curve at this point is changed to one with curvature described by the exponent $(1 - \alpha)/\beta$. The classical and nonclassical three-phase equilibrium curves are compared in Fig. 6. [We note that locating this curve in an appropriate experimental system may be one of the simplest ways of measuring both the exponent $(1 - \alpha)/\beta$ and the "out-of-plane" exponent $(1 + \beta)/\beta$—the latter has apparently has been measured yet by *any* method.]

Besides the expected flattening at the critical points P' and Q', the nonclassical curves in Figs. 6a and 6b also show a deviation from the classical shape as the noncritical phases P_n and Q_n (in equilibrium with the critical phases P' and Q', respectively) are approached along the space curve. We at present believe that these deviations are artifacts of our formulation, but it is interesting to note that Fisher and Sarbach[10] have suggested that similar

deviations may occur in real fluids (this suggestion is based upon the tricritical phase behavior of the spherical model).

As we have mentioned, we have yet to explicitly calculate the densities except on a number of important sample field-space trajectories. We note that if the densities are known analytically on certain manifolds (for example, on the manifolds $a_4 = 1$ and $a_4 = -1$), the tricritical scaling properties of F' allow those results to be extended to the whole field space (this was pointed out by Griffiths). Yet, despite the fact that our knowledge of the details of this model is incomplete, we have in this paper been able to make a number of predictions which may now be critically tested by experiment.

There is one detail of our formulation which, while completely unrelated to the question of nonclassical scaling, touches upon a topic of recent theoretical interest. Fisher and Sarbach[10] have pointed out that there are a number of dimensionless "tricritical amplitudes" which are predicted to be zero by classical theory but known to be nonzero in various experimental systems other than in ordinary fluid mixtures (where they have not been measured at all) and in some model calculations. The most significant of these discrepancies may be expressed, in the language of this model, as the fact that, classically, the curve ρ_2 vs. a_4, say, on the manifold $c_1 = R_1 = R_2 = 0$ ($a_4 < 0$) is tangent to the corresponding curve on the manifold $c_2 = c_3 = R_1 = 0$ ($a_4 > 0$) at the point of intersection, the tricritical point ($a_4 = 0$), whereas in reality they are not tangent. These curves are tangent in the present nonclassical model, but this is only due to the fact that we have inadvertently chosen g_0 such that $g_0 = g_1 = g_2$ on the $c_1 = R_1 = R_2 = 0$ manifold. The function g_0 may be altered [for example, a term of the form

$$k_3(c_1 - c_2)^{2m}(c_1 - c_3)^{2m}(c_2 - c_3)^{2m}$$

might be inserted into the definition of g_0 introduced previously, with n in Eq. (46) chosen such that $2n = 3m$, with m a positive integer] to produce (qualitatively) the experimental result, but the fact that our formulation is equivocal on this question suggests that there remains a level of detail of these models yet to be explored.

5. CONCLUDING REMARKS

The nonclassical equation of state developed in the preceding section to describe phase behavior near a tricritical point may be viewed as the embodiment of the tricritical scaling hypotheses of previous authors[4,5] in an explicit free energy formulation. Perhaps the most important result of this development is that in this formulation, despite its algebraic complexities, the mechanism mediating the competition between critical scaling and tricritical scaling, and the resulting crossover from one scaling region to the other,

takes a very simple form, i.e., the terms in the density relations bearing non-classical critical exponents simply cancel out as the tricritical point is approached.

Our development of the nonclassical free energies introduced here originated with the question of how and to what extent the predictions of classical theory should be modified to take into account the nonclassical critical scaling behavior characteristic of real fluid mixtures. We have provided a partial answer to this question, in that the qualitative differences between the phase diagrams of the classical and nonclassical formulations certainly imply the type of discrepancies we might expect to see between the predictions of classical theory and the behavior of real fluid mixtures.

If these nonclassical equations of state do, in fact, represent a significant improvement over the classical formulations upon which they are based, then the development of our "rescaling technique" to the point where it could be applied to classical formulations generally would be a valuable theoretical contribution. We do not at present know how to proceed with such a development, but it is apparent that our interpretation of the basic nonclassical scaling hypothesis of the technique in terms of a particular parametric form is probably too narrow a point of view to form a basis for this development. We can only suggest that what is probably required is a direct identification between the variables which appear in the scaling hypothesis and the topological features of the classical phase diagram. Such an identification would then be independent of the often arbitrary choice of parametrization of the classical formulation in question.

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