Universality and Interfaces at Critical End Points

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At a critical end point a critical phase coexists with a *non*critical phase α and singularities arise beyond those on the associated critical line. New *universal* amplitude ratios are defined for the shape of the α phase boundary and for the noncritical surface tensions near end points. A postulated correspondence with wall/surface criticality leads to predictions for general dimension d that are exact at (and near) $d=2$ and for $d\geq 4$ (where mean-field theory applies) and yield experimentally testable estimates for $d=3$.

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Consider a normal critical point of binary fluid demixtion or gas-liquid condensation (order-parameter symmetry, $n=1$), of a superfluid ($n=2$), or of an isotropic ferromagnet ($n=3$), with a critical temperature $T_c(g)$, where g represents a *nonordering field* such as the pressure, or the chemical potential of an extra species, etc. If, say, the specific heat exhibits a singularity $A_\pm(g)|t|^{-\alpha}$ as $t\equiv[T-T_c(g)]/T_c(g)\to 0\pm$, then the ratio $A_+(g)/A_-(g)$ is, very generally, a *universal* number, independent of g; for example, $A_+/A_-\simeq 0.523$ for $n=1$ in $d=3$ dimensions.[1] Such amplitude ratios are of interest since, like the critical exponents, α, β, ν, etc., they characterize the universality classes of critical behavior.

Now if the field g is changed sufficiently, one often encounters a *critical end point,* (T_e,g_e), at which the critical line $T_c(g)$ meets and is truncated by a first-order phase boundary beyond which the system realizes a new, disordered, noncritical phase, say, α, typically a vapor;[2] see Fig. 1(a).[3] It is commonly accepted that the critical exponents and amplitude ratios defined *on* the critical line are no different than *at* the end point (although this has rarely been carefully checked experimentally or theoretically[4]). To our knowledge, however, it has not previously been noted that critical end points exhibit universal singular behavior *beyond* that observable at ordinary critical points. The purpose of this Letter is to elucidate some of these new features and to provide quantitative estimates of the associated amplitude ratios that may be tested experimentally or in simulations.

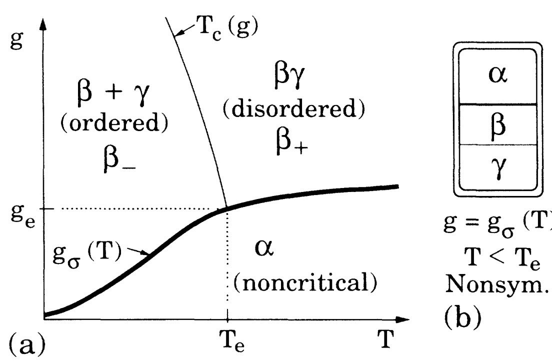

FIG. 1. (a) A critical line $T_c(g)$, an end point (T_e,g_e), and a first-order transition boundary $g_\sigma(T)$, where g is a nonordering field, like the pressure. (b) Coexisting fluid phases below a nonsymmetric critical end point.

Two fundamentally distinct cases arise: *symmetric* **S** and *nonsymmetric* **N**. Case **N** represents, e.g., fluid mixtures in which, below $T_e=T_c(g_e)$, a vapor phase α may *coexist,* on what is then a *triple line* $g_\sigma(T)$ with two distinct liquid phases, say, β and γ, unrelated by any symmetry operation; see Fig. 1(b). Above $T_c(g)$ the liquid phases merge into a single disordered phase, say, $\beta\gamma$. In case **S**, exemplified by a binary alloy ($n=1$), a superfluid ($n=2$), or a ferromagnet ($n=3$), the ordered phase below T_e, say, β_-, realizes a broken symmetry absent in the new *spectator* phase, α. In other words, the ordering field $\vec{h}$, which selects the "sense" of β_- below T_c, does *not* couple linearly to the free energy of the phase α.[3]

Perhaps the simplest novel aspect of a critical end point is that the phase boundary $g_\sigma(T)$ itself should be singular at T_e. Indeed, naive thermodynamic arguments[5] yield

$$g_\sigma(T)-g_0(T)\approx -X_\pm|t|^{2-\alpha} \text{ as } T\to T_e\pm\ , \qquad (1)$$

with $g_0(T)=g_e+g_1t+\cdots$ analytic, $X_\pm>0$, and, furthermore, a universal ratio $X_+/X_-=A_+/A_-$. This conclusion has been checked theoretically in explicit calculations for the $n\to\infty$ or spherical-model limit for systems of general dimensionality d.[6] Both short-range interactions and long-range power-law couplings are encompassed.[6] Experimental tests should be feasible; note that when g is the pressure p and $\alpha>0$, one finds the divergence

$$\frac{d^2p_\sigma}{dT^2}\approx -\frac{A_\pm|e_0|^{2-\alpha}}{(v_e-v_c)T_e}|t|^{-\alpha}, \qquad (2)$$

where $A_\pm$ is the amplitude of the constant-pressure molar heat capacity on the critical locus near the end point, while $e_0=1-(dT_c/dp)_e(dp_\sigma/dT)_e$ and v_e and v_c are the end-point molar volumes of the spectator and critical phases, respectively.

The droplet picture of condensation[7-9] implies an essential singularity in all derivatives of the thermodynamic potential, $\pi(T,g)$, when the phase boundary is approached in the α phase, i.e., as $z \equiv g - g_\sigma(T) \to 0-$. More concretely, suppose α is a vapor, g is the chemical potential, and the free energy of a droplet of $l \gg 1$ particles varies analytically as[7,8]

$$F_l(T)/k_BT \approx l f_\infty(T) + l^\sigma f_\sigma(T) + \tau \ln l + \cdots, \tag{3}$$

with $\sigma = 1 - 1/d$, describing bulk, surface, and closure contributions. Then the essential singularity is characterized by a cut along the positive real axis of the complex z plane with a discontinuity that vanishes as[7]

$$\Delta\left(\frac{\partial^j}{\partial T^j}\frac{\partial^k}{\partial g^k}\pi\right) \propto i e^{-c(T)/z^{d-1}}/z^{\lambda(j,k)}, \tag{4}$$

when $z \to 0$, with $c(T) > 0$ analytic,

$$\lambda(j,k) = d(k + j + \tfrac{1}{2} - \tau) + \tfrac{1}{2}, \tag{5}$$

and a correction factor $1 + c_1 z + c_2 z^2 + \cdots$.

Near an end point, however, the droplets become *critical* and the arguments must be reconsidered. Finite-size scaling[8] shows that (3) must be modified by adding a singular part[10]

$$\Delta F_l/k_BT \approx U(t l^{1/d\nu}) + \eta^* \ln l, \tag{6}$$

where ν is the standard correlation length exponent while, in general, $\eta^* \neq 0$. (Increments Δf_∞ and Δf_σ are also entailed.) The scaling function $U(x)$ is analytic but varies as $U_\infty^\pm x^{d\nu} + U_1^\pm x^{(d-1)\nu} - d\nu\eta^* \ln|x|$ when $x \to \pm\infty$, where hyperscaling, with $d\nu = 2 - \alpha$, is implied.[11] The previous reasoning[7,8] then recaptures the result (1) for the phase boundary. Furthermore, the form (4) is also *not* changed. However, just *at* the end point T_e the exponent λ becomes $\lambda_c = \lambda - d\eta^*$ and new terms $O(U'(0)z^{(1-\alpha)/\nu})$ appear in the correction factor.

Beyond bulk properties, of particular interest at a critical end point are the *non*critical interfaces and their tensions:[12,13] $\Sigma_{\alpha|\beta_\pm}(T)$ for case **S** and $\Sigma_{\alpha|\beta}$ and $\Sigma_{\alpha|\beta\gamma}$ for case **N** [see Fig. 1(b)]. Note that the usual *critical* interfacial tension below T_e vanishes as[12]

$$\Sigma_{\beta|\gamma}(T) \approx K|t|^\mu \quad (n=1), \tag{7}$$

where $\mu = 2 - \alpha - \nu$ is the surface-tension exponent obeying $\mu = (d-1)\nu$ for $d \le 4$ and $\mu = \frac{3}{2}$ for $d > 4$. For $n \ge 2$ one may define the amplitude K analogously by replacing $\Sigma_{\beta|\gamma}$ by $k_BT(\Upsilon/k_BT)^\psi$ with $\psi = (d-1)/(d-2)$ (for $d \le 4$), where $\Upsilon(T)$ is the appropriate *helicity modulus.*[14]

Now if $\Sigma_0(T) > 0$ is a suitable analytic background term, scaling dictates

$$\Delta\Sigma_{\alpha|\beta_\pm}(T) \equiv \Sigma_{\alpha|\beta_\pm} - \Sigma_0 \approx K_\pm |t|^\mu \quad (\mathbf{S}) \tag{8}$$

and similarly for $\Sigma_{\alpha|\beta}$ and $\Sigma_{\alpha|\beta\gamma}$ (**N**). The *amplitude ratios,*

$$P = (K_+ + K_-)/K \quad \text{and} \quad Q = K_+/K_-, \tag{9}$$

then serve to characterize critical end-point behavior. Although apparently not remarked previously, *both* these ratios should be *universal* (at least for $d < 4$) and accessible to experimental study. [Note that $K_\pm/K = P/(1 + Q^{\mp 1})$.]

Widom and co-workers[12] have studied the end-point tensions within classical, square-gradient, Landau-van der Waals theory (carried to m^6 in the order parameter m). Implicit in their analysis are the results

$$P = -\tfrac{1}{2}(\sqrt{2} - 1) \simeq -0.207, \quad Q = -\sqrt{2} \quad (\mathbf{N}), \tag{10}$$

and

$$P = \tfrac{1}{2}, \quad Q = 0 \quad (\mathbf{S}), \tag{11}$$

which, with $\mu = \frac{3}{2}$, should be valid for $d > 4$. Furthermore, the universality of these values has been checked[13,15] within mean-field theory including orders $m^7, m^8, \ldots$. The leading correction term to (8) varies as t^2 for $\Sigma_{\alpha|\beta}$ but as $t^2 \ln t$ for $\Sigma_{\alpha|\beta\gamma}$.[13,15] The negative signs in (10) are, perhaps, surprising; they imply a *cusp* in the interfacial energy and seem to *disagree* with available experiments on fluids.[12]

To go further and obtain results for $d < 4$ we first explore the rather natural hypothesis, $\mathbf{\Omega}$, that *the spectator phase α can be replaced by a rigid wall ω.*[16] This is reasonable as $t \to 0$ since the fluctuations in α are noncritical; evidently, however, $\mathbf{\Omega}$ cannot reproduce (1) nor does it allow for displacements of the free $\alpha|\beta$ interface. Nevertheless, within mean-field theory for walls (the wall being endowed with a surface field,[17] h_1, etc.) one discovers[15] that P and Q do retain the *same universal values* as at an end point. More explicitly, the singularities of $\Sigma_{\alpha|\beta}$, etc., match those of the wall free energies, $\Sigma_{\omega|\beta}$, etc., of a semi-infinite bulk phase near its ordinary bulk critical point.[15] The cases **S** and **N** correspond to $h_1 = 0$ and, say, $0 < h_1 \le \infty$ and can be identified with the *ordinary* and *extraordinary* surface transitions, respectively.[15,17] The same scaling forms are then reproduced although the $t^2 \ln t$ end-point correction is *not* found.

Accepting $\mathbf{\Omega}$ and utilizing renormalization-group field-theoretic calculations for the wall problem[18] when $\epsilon = 4 - d \to 0+$ yields the novel prediction

$$Q(d) = \tfrac{1}{4}\pi\sqrt{2}n\epsilon/(n+8) + O(\epsilon^2) \quad (\mathbf{S}, h_1 = 0). \tag{12}$$

Regrettably, no further applicable ϵ-expansion results seem currently available.

In $d = 2$ dimensions one has $\mu = 1$ for $n = 1$ and $\Sigma_{\beta|\gamma}$ vanishes simply as $K|t|$; however, the *wall* free energies of $d = 2$ Ising models vary *logarithmically* as[19]

$$\Sigma_{\omega|\bullet}(T) = \Sigma_c + K_l t \ln|t|^{-1} + K_\pm |t| + \cdots, \tag{13}$$

so that Q is no longer well defined. Nevertheless, one may look for universality over various Ising lattices. For square lattices (with both axial and diagonal walls) and for triangular and honeycomb lattices[19] we find

$$P=\tfrac{1}{4}, \quad P_l \equiv K_l/K = 1/4\pi \quad (d=2; \mathbf{N}, h_1=\infty), \tag{14}$$

and

$$P=\tfrac{1}{4}, \quad P_l = -1/4\pi \quad (d=2; \mathbf{S}, h_1=0) \tag{15}$$

—results previously unnoticed. We speculate, on the basis of Ω, that these values will characterize both real and model Ising-like end points in $d=2$ dimensions.

The unexpected logarithmic behavior (13) can be understood as follows. Suppose $G(T;d)$ is some property displaying a critical singularity with exponent $\zeta(d)$ *and* an analytic background piece [like $\Sigma_{\alpha|\beta}(T)$ but *unlike* $\Sigma_{\beta|\gamma}(T)$ which vanishes identically for $T>T_c$]. Then, when $\zeta \equiv m + \Delta\zeta(d)$ is close to an integer m, experience teaches[20] that the singular part should vary as $-G_l t^m(|t|^{\Delta\zeta}-1)/\Delta\zeta$, representing a "resonance" between singularity and background. When $\Delta\zeta \to 0$ this yields $\Delta G \approx G_l t^m \ln|t|^{-1}$. On these grounds (see also below), we conclude that as d varies one has

$$K_\pm(d)/K(d) \approx \mp P_l/\Delta\mu + \tfrac{1}{2}(P \pm p_0) + p_1^\pm \Delta\mu, \tag{16}$$

when $\Delta\mu \equiv \mu(d) - 1 \to 0$, P_l and P being given by (14) or (15).

Now $\mu(d)$ is known to $O(\epsilon^5)$ and varies almost linearly for $2 \le d \le 4$ with[1] $\mu(3) \simeq 1.264$. Thus $K_\pm/K$ can be estimated roughly for all d simply by matching (16) near $d=2$ and $d=4$.[21] The resulting predictions for $Q(d)$ are shown in Fig. 2; $P(d)$ is predicted to vary linearly with μ. Note that Q always approaches -1 as $d \to 2$; but that in case **S**, Q changes sign via an unexpected *pole* at $d \simeq 2.6$. In the symmetric, three-dimensional case the approximation gives

$$Q \simeq 0.49, \quad P \simeq 0.38 \quad (d=3; \mathbf{S}, n=1). \tag{17}$$

Then simple proportionality, using (12), suggests $Q(d=3) \simeq 0.9$ for $n=2$; this value should describe the surface tension of superfluid ^{4}He above and below the λ point. The experiments of Magerlein and Sanders[22] seem consistent with this approximation but further observations and analysis would be worthwhile.

For the fluid case (**N**, $n=1$) one finds[21] $Q(d=3) \simeq -0.98$ and $P(d=3) \simeq 0.01$. The negative sign of Q, as found for $d \ge 4$, seems trustworthy; further experimental tests are surely called for. However, especially in the absence of the analog of (12), the *magnitude* must be regarded as dubious. One route towards an improved estimate would be to derive $O(\epsilon^2)$ expansions for P and Q. These would allow the introduction of a $(\Delta\mu)^2$ term in (16) (and yield a nontrivial variation for P). However, the necessary calculations are technically difficult.

We have,[15] instead, undertaken a study which utilizes a novel *nonclassical* but local functional equation for the order-parameter profile. This generalizes, in a nontrivial

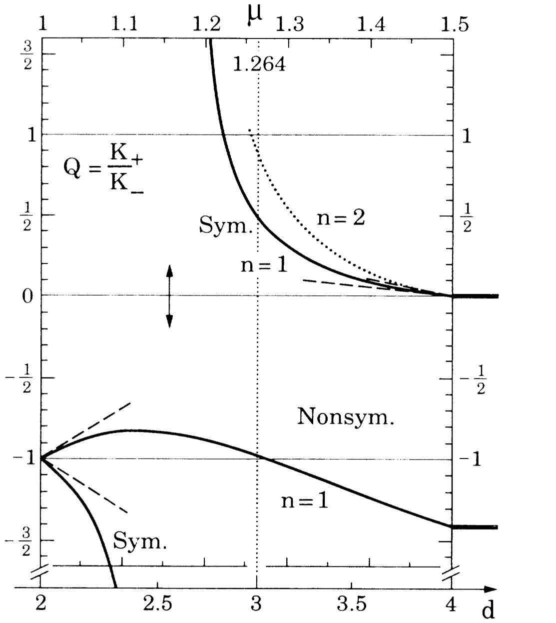

FIG. 2. Variation of the universal amplitude ratio $Q(d)$ with μ and d. The solid curves are approximations accurate near $d=2$ and 4, while the dashed lines represent exact asymptotic behavior. For $d=3$, see also Eq. (18).

fashion, a nonclassical functional equation advanced by Fisher and de Gennes[23] that made various surprising predictions, since verified,[24] that go *beyond* simple scaling. The details will be described elsewhere;[15] here we summarize briefly the main conclusions: (i) The hypothesis Ω, the wall/end-point equivalence, is justified for general, nonclassical equations of state and correlation functions; (ii) the crucial role of the required analyticity properties of the scaling functions for the equation of state, etc., is demonstrated;[25] (iii) the logarithmic form (13) and its analog for μ any integer is derived generally; (iv) likewise the amplitude variation (16) is established; and (v) by utilizing parametric representations of the equation of state,[8] including new "trigonometric" and "interpolated linear models,"[15] explicit numerical estimates for $P(d)$ and $Q(d)$ are computable that are consistent with the exact ϵ expansion and $d=2$ data and with the best-series estimates for $d=3$.[1] Explicitly, a first calculation[15] yields the improved estimates

$$Q \simeq -0.82, \quad P \simeq 0.1 \quad (d=3; \mathbf{N}, n=1), \tag{18}$$

which we believe will prove fairly accurate.

Finally, we point out the general interest of the hypothesis Ω and the value of checking it further. Clearly, it does not allow for the capillary-wave fluctuations of the $\alpha|\beta$ interface which are always present for $d<3$. In $d=3$ it is possible that Ω applies when $\alpha|\beta$ is smooth at the end point but not when it is rough. Can the *special* wall transition[17] be identified as some class of end-point behavior?

In summary, we have highlighted various novel universal features, especially amplitude ratios, that characterize symmetric and nonsymmetric critical end points. Theories providing quantitative estimates for $d=2$ and 3, that are susceptible to test by experiment and simulation, have been sketched.

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[2]Context will serve to avoid confusion between the exponents α,β,γ and the phases labeled α, β, and γ.

[3]The (T,g) plane in Fig. 1(a) should be understood as the manifold of zero ordering field, $\vec{h}=0$, in the "full" phase space $(T,g,\vec{h})$. We may suppose it is smooth as a function of thermodynamic fields.

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