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Phase boundaries near critical end points. I. Thermodynamics and universality

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The vicinity of a critical end point is analyzed in order to reveal singularities arising in the form of the first-order phase boundary to the noncritical phase. Phenomenological arguments are presented and critically assessed that directly relate the nonanalytic behavior of the phase boundary to universal features of the bulk thermodynamics on the associated critical line. Explicit values are given for universal amplitude ratios describing the boundary for various types of criticality.

I. INTRODUCTION

At a *critical end point* a critical line (or lambda line) is truncated by meeting a first-order phase boundary delimiting a new noncritical thermodynamic phase, α, quite distinct from the phases, say, β and γ, associated with the criticality. Critical end points are, in fact, ubiquitous thermodynamic features observed especially frequently in studies of the phase equilibria of binary fluid mixtures and other multicomponent systems such as alloys, liquid crystals, etc. However, they occur also in pure systems: For example, the ferromagnetic Curie points and antiferromagnetic Néel points of elements such as nickel, iron, and chromium, or compounds such as manganese fluoride, are critical end points when observed under their crystalline vapor pressures—α being the vapor phase. The lambda line bounding the superfluid phase of ^{4}He exhibits two end points: The lower end point is the standard λ point observed under helium vapor pressure; at the upper end point the noncritical "spectator" phase, α, is the solid crystal. In magnetic systems end points are often found as the external magnetic field is varied in magnitude and direction. More generally, critical end points are intimately associated with the vicinity of tricritical points in thermodynamic spaces of appropriate dimensions.[1]

Despite their ubiquity, critical end points have been little studied for their own sake either from a general phenomenological standpoint or within specific theoretical models.[2] However, it has been pointed out recently[3] that even the bulk thermodynamics of an end point should display new critical singularities, not observable on the associated critical line, which, furthermore, ought to be characterized by various *universal* parameters. In particular, the phase boundary between the α and β or γ phases should exhibit nonanalyticities as the end point is approached, reminiscent of the singularities in the critical lines (or surfaces) predicted[1] and observed[4] in bicritical phase diagrams. More concretely, for the simplest critical end point situation depicted in Fig. 1, in which g may be taken as, say, the pressure, it was asserted[3] that the phase boundary, $g_\sigma(T)$, should have a *divergent curvature* obeying

$$\frac{d^2 g_\sigma}{dT^2} \approx -X^0_\pm / |T-T_e|^\alpha , \tag{1.1}$$

as T approaches the end point temperature T_e from above or below. Here α is the critical exponent describing the specific heat singularity (at constant g) on the critical line above $g_e = g_\sigma(T_e)$ and is supposed positive as for Ising-like (or $n=1$) systems in $d=3$ dimensions.[5] Furthermore, the amplitude ratio X^0_+/X^0_- should be universal, independent of the details of the end point (up to the universality class of the critical line) and equal to A_+/A_- where $A_+(g)$ and $A_-(g)$ are the amplitudes of the specific heat singularity observed on the critical line. This ratio in turn should be universal (and so independent

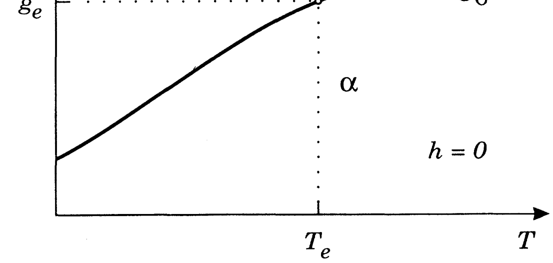

FIG. 1. Illustration of a critical end point at the join of a critical line λ, $T=T_c(g)$, and a first-order phase boundary, $g=g_\sigma(T)$, which separates the noncritical spectator phase α from the coexisting phases β and γ (or ordered phase $\vec{\beta}_-$) and from the disordered phase $\beta\gamma$ (or β_+).

of g) by the general theory of critical phenomena; for Ising-like systems one has[5] $A_+/A_- \simeq 0.523$

Our aim in the present work is to explain and assess this prediction and extend it to other universal features of the phase boundary, in particular, those observable when one departs from the coexistence surface and its smooth continuation (which corresponds to the plane of Fig. 1). We find, at the phenomenological level, that the different universal ratios characterizing the phase boundary can all be related to bulk universal amplitude ratios[6] combined with certain geometrical parameters of the critical end point.[7] On that basis we present explicit predictions for various types of critical end point including classical or mean-field theory end points and those in spherical models ($n \to \infty$) with short-range and long-range forces.[8]

To check these predictions beyond mean-field theory, however, requires the analysis of specific models which actually have end points! To that end, Parts II and III of this series will be devoted to extended spherical models, of a type introduced by Sarbach and Schneider,[9] which display *tri*critical points and, as we show in detail, also have *nonclassical* critical end points. These analyses do verify the conclusions of the phenomenological arguments expounded here. Nevertheless, the results are not, in general, beyond question so it remains of interest to explore nonclassical critical end points in other models. Experiments to check our predictions on favorable systems, such as superfluid helium, are also called for.

In outline the remainder of this paper is as follows: Considerations pertaining to the nature of the coexistence surface between the β and γ phases and its continuation are presented in Sec. II. The appropriate universal scaling description of criticality near a critical line is recalled in Sec. III. The classical argument for obtaining phase boundaries by matching free energies of distinct phases is assessed in Sec. IV. Accepting the plausible but uncertain conclusions of this argument the behavior of the phase boundary to the spectator phase α is analyzed in temperature and field variables in Sec. V. Various new universal amplitude ratios are formulated and specific predictions for some models are listed. Section VI summarizes the conclusions briefly.

II. CRITICAL LINE AND THE COEXISTENCE SURFACE

It is helpful to recapitulate, first, the thermodynamics associated with a critical line. To this end, let g in Fig. 1 denote a nonordering thermodynamic field, like the pressure, a chemical potential, or a component of the magnetic field, that modifies the critical temperature, $T_c(g)$, but does not change the universality class of the continuous phase transition. We may safely suppose that the critical line, λ, is a smooth and, indeed, analytic function of $g > g_e$. For a full thermodynamic description one must also recognize the existence of an ordering field h that destroys the transition. For an Ising-like or $n=1$ system beneath $T_c(g)$ two distinct phases, β and γ, may coexist when $h=0$. Above $T_c(g)$ these merge into a single $h=0$ phase which we call $\beta\gamma$; however, imposition of a nonzero field h enables one, in the standard way, to convert phase β smoothly and, indeed, *analytically* as regards the g, T, and h variations of all thermodynamic properties, into phase $\beta\gamma$ and, thence, moving around the critical line, into phase γ: see Fig. 2.

If the order parameter, M, of the transition is more complicated than a density or concentration, as in an n-vector system with $n=2,3,\ldots,$ the full ordering field is no longer a simple scalar; rather it is, for example, an n-component vector $\vec{h}$. Likewise the ordered phase below $T_c(g)$, say $\vec{\beta}_-$, will have some *sense* (e.g., of a vectorial character) determined by the sense of $\vec{h}$ in the limit $|\vec{h}| \to 0$. We may then identify the phases β and γ as phases $\vec{\beta}_-$ and $\vec{\beta}'_-$ with *opposite* senses. Likewise, we may let h denote a single component of $\vec{h}$ (the others vanishing identically). The $\vec{h}=0$ disordered phase β_+ above $T_c(g)$ has no sense and may be identified with the $n=1$ phase $\beta\gamma$. Then one may ignore the distinction between $n=1$ and other universality classes except for remembering, when necessary, any exact symmetries associated with $\vec{h}$ and there consequences, such as Goldstone-mode or spin-wave singularities on the phase boundary.

When the system under study has a special global symmetry, as a ferromagnet with respect to a magnetic field or a superfluid under an overall gauge transformation, the *coexistence condition* $h=0$ has an unambiguous physical meaning for *all* g and T (even if the phases β and γ, etc., are not realized). More generally, however, in unsymmetric situations the coexistence surface, ρ (see Fig. 2), which is bounded by λ, the critical line $T=T_c(g)$, and, if present, by τ the triple line $g=g_\sigma(T)$, must be regarded as a *curved manifold* in an underlying thermo-

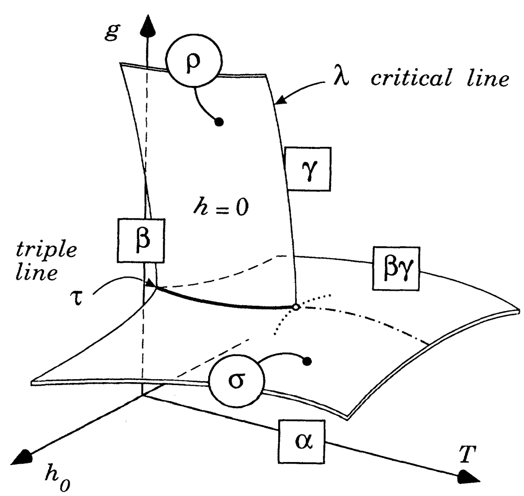

FIG. 2. The full thermodynamic space (T,g,h_0) showing an unsymmetrical critical line λ terminating at a critical end point (open circle), and the corresponding coexistence surface ρ, bounded by λ and by the associated triple line τ, where ρ meets the spectator phase boundary, σ. The dot-dashed line on σ represents the intersection with the extended coexistence surface $\tilde{\rho}$ specified by $h=0$.

dynamic space (g,T,h_0). Here h_0 is the basic thermodynamic field corresponding to h but entering directly into the original thermomechanical specification of the system. Away from the boundaries of ρ, λ, and τ, we may safely suppose (A) that the manifold ρ is fully analytic; in other words we can regard h as an analytic function of g, T, and h_0 on ρ. We may also safely suppose (B) that ρ has a unique tangent plane everywhere including on λ and τ.

Beyond that, however, we will *assume* (C) that the coexistence manifold ρ is sufficiently *smooth on its boundaries* λ and τ that it can be *extended* with insignificant ambiguity into a manifold $\tilde{\rho}$, defined for general g and T and analytic away from λ and τ, the critical and triple lines. More concretely, we will assume that the curvature and further T, g, and h_0 derivatives of ρ (and hence of $\tilde{\rho}$) are well defined on the boundaries up to some order $N>2$, the appropriate value of N depending on the particular context. More strongly, one might wish to assume—although we will *not* need to—that ρ is *analytic* on its boundaries and so may be *analytically* continued to define the extended manifold $\tilde{\rho}$.

While very plausible at the phenomenological level, the smoothness and, even more, the analyticity of the coexistence surface ρ *through* the critical line λ (and *through* the triple line τ) *cannot* be regarded as obviously correct from the viewpoint of statistical mechanics. Indeed, if, as we argue, the curvature of $g_\sigma(T)$ diverges in accord with (1.1), why should a similar divergent curvature not arise in the coexistence surface ρ on approach to λ? It might, in fact, be the case that for certain choices of thermodynamic fields, g and h_0, such a singularity does arise while for others of a more optimal character it can be avoided. For systems such as the penetrable-sphere model,[10] where there is some underlying or hidden symmetry, analogous to the manifest symmetries discussed above, such a guess is reasonable. We will not pursue the issue further here. Nevertheless, it is worth noting that some experimentally observed disagreement with the predictions we make could, in principle, reflect on assumption (C).

In summary, we will assume that the ordering field h is a smooth function of T, g, and h_0 everywhere, including on the critical line, λ. Then we may use h in place of h_0, which will not appear further in our analysis (although the dependence of h on h_0 may need to be recalled in interpreting experiments). The coexistence surface ρ and its extension $\tilde{\rho}$ are thence simply described by $h=0$. As mentioned, we also suppose that $T_c(g)$ is analytic away from the end point.

III. CRITICAL-LINE THERMODYNAMICS

To characterize the critical behavior in the space (T,g,h) as the critical line λ is approached we consider the appropriate thermodynamic potential or Gibbs free energy, say $G_{\beta\gamma}(g,T,h)$. General scaling and renormalization group principles indicate that there should be an analytic background piece, $G_0(g,T,h)$, and a singular piece which embodies the leading critical singularities and the corrections to scaling.[11] To give an explicit form for $G_{\beta\gamma}$ it is most useful to introduce nonlinear scaling fields

$$\tilde{t}(g,T,h)\approx[T-T_c(g)]/T_e, \quad \tilde{h}(g,T,h)\approx h \ , \tag{3.1}$$

where T_e enters here only as a convenient reference temperature and the "asymptotically equals" symbol entails $T\to T_c(g)$ and $h\to 0$. The functions $\tilde{t}$ and $\tilde{h}$ are smooth, if not actually analytic functions of their arguments and embody any exact symmetries in h.

If α is the specific heat exponent, Δ is the gap exponent, and $\theta\equiv\theta_4,\theta_5,\ldots$ are the correction-to-scaling exponents,[12] we then have

$$G_{\beta\gamma}(g,T,h)=G_0(g,T,h)-Q|\tilde{t}|^{2-\alpha}W_\pm\left[\frac{U\tilde{h}}{|\tilde{t}|^\Delta},U_4|\tilde{t}|^\theta,U_5|\tilde{t}|^{\theta_5},\ldots\right] , \tag{3.2}$$

where Q, U, U_4, and U_5 are smooth and/or analytic functions of g, T, and h. we suppose that none of the irrelevant variables are dangerous[12] so that the asymptotic scaling function,

$$W_\pm^0(y)\equiv W_\pm(y,0,0,\ldots) \ , \tag{3.3}$$

is well defined and may be *normalized* by $W_+^0(0)=1$. The two branches of the scaling function $W_\pm(y,\ldots)$ must satisfy matching conditions as $y\to\pm\infty$ which ensure the analyticity of $G_{\beta\gamma}$ for all $h\neq 0$. For simplicity we write these conditions for a symmetric (under $h\to -h$) critical point as

$$W_\pm^0(y)\approx W_\infty|y|^{(2-\alpha)/\Delta}[1\pm W_1|y|^{-1/\Delta}+W_2|y|^{-2/\Delta}\pm\cdots] \ . \tag{3.4}$$

Finally we note that the normalized scaling function will be *universal.*

In the standard way we now define various critical amplitudes $A_\pm,B,\ldots$. First, for the specific heat at constant g,

$$\mathcal{C}(g,T)\approx T_c^{-1}A_\pm(g)|\tilde{t}|^{-\alpha}, \quad \tilde{t}\to 0\pm \ , \tag{3.5}$$

where, in case $\alpha<0$, $\mathcal{C}$ denotes only the singular part of the specific heat;[11] second, for the spontaneous order parameter

$$M_0(g,T)\equiv-\lim_{h\to 0}\frac{1}{2}\left[\frac{\partial G}{\partial h}(h)-\frac{\partial G}{\partial h}(-h)\right]$$
$$\approx B(g)|\tilde{t}|^\beta, \quad \beta=2-\alpha-\Delta \ ; \tag{3.6}$$

then, for the critical isotherm, $T=T_c(g)$ at fixed g,

$$\Delta M(g,h)=M(g,T_c,h)-M_c(g)$$
$$\approx\pm B_c(g)|h|^{1/\delta}, \quad \beta\delta=\Delta \ , \tag{3.7}$$

where asymptotic symmetry in $\pm h$ is again assumed for convenience; finally for the susceptibilities above and below $T_c(g)$,

$$\chi(g,T) \equiv -\frac{\partial^2 G}{\partial h^2} \approx C_{\pm}(g)|\tilde{t}|^{-\gamma}, \; \gamma = 2-\alpha-2\beta . \quad (3.8)$$

From (3.2) we easily find

$$A_{\pm}(g) = (2-\alpha)(1-\alpha)W_{\pm}(0)Q[g,T_c(g),0] , \quad (3.9)$$

$$B(g) = W'_{-}(0)Q[g,T_c(g),0]U[g,T_c(g),0] , \quad (3.10)$$

and similarly for $B_c(g)$ and $C_{\pm}(g)$, where, for brevity, we have dropped the superscript 0 on $W_{\pm}$, etc., here and in the following few formulas.

Then we may introduce various dimensionless ratios of the critical amplitudes which, since they depend only on $W^0_{\pm}(y)$, are universal. Specifically we consider

$$\frac{A_+}{A_-} = \frac{W_+(0)}{W_-(0)} \quad \text{and} \quad \frac{C_+}{C_-} = \frac{W''_+(0)}{W''_-(0)} , \quad (3.11)$$

where the primes denote differentiation (with respect to the argument y); and

$$\Theta_1 \equiv \frac{A_+C_+}{B^2} = \frac{(2-\alpha)(1-\alpha)W_+(0)W''_+(0)}{[W'_-(0)]^2}, \quad (3.12)$$

$$\Theta_2 \equiv \frac{A_+B_c^{\delta}}{B^{\delta+1}} = \frac{(2-\alpha)^{1+\delta}(1-\alpha)W_+(0)W^{\delta}_{\infty}}{\Delta^{\delta}[W'_-(0)]^{1+\delta}} . \quad (3.13)$$

It may also be useful to consider the derived ratios

$$\Theta_3 \equiv B^{\delta-1}C_+/B_c^{\delta} = \Theta_1/\Theta_2 , \quad (3.14)$$

for systems in which $A_+ = 0$ as in mean field theory, and

$$\Theta_4 \equiv |A_+|^{\delta-1}C_+^{\delta+1}/B_c^{2\delta} = |\Theta_1|^{\delta+1}/\Theta_2^2 . \quad (3.15)$$

Of course, additional universal amplitudes involving $W'''_{\pm}(0), \ldots$ and the W_k in (3.4) may be readily defined but are harder to observe experimentally. Further universal ratios enter when the corrections to scaling are explicitly studied; however, we will leave aside the corrections until Part III.

IV. SPECTATOR PHASE BOUNDARY

By definition of the spectator phase, α, it is noncritical, with a finite correlation length, throughout the vicinity of the critical end point at $(g,T,h)=(g_e,T_e,0)$. Hence its free energy, $G_\alpha(g,T,h)$, should be analytic everywhere except, possibly, *on* the phase boundary σ which we will specify by $g = g_\sigma(T,h)$. Our aim, of course, is to determine any singularities of the function $g_\sigma(T,h)$ at $(T_e,0)$. Now, according to the traditional Gibbsian view of equilibrium thermodynamics,[3] both the free-energy functions $G_{\beta\gamma}(g,T,h)$ and $G_\alpha(g,T,h)$ should continue smoothly and, presumably, analytically beyond the boundary σ to define "metastable extensions" in the regions where the other free energy is actually lower, so describing the stable phase. If that is accepted the phase boundary can be derived simply by equating the suitably continued free energies and solving the resulting equation, namely,

$$G_\alpha(g_\sigma(T,h),T,h) = G_{\beta\gamma}(g_\sigma(T,h),T,h) . \quad (4.1)$$

However, this view is contradicted by arguments based on the droplet picture of the condensing phases,[3,13,14] which have been supported, more recently, by rigorous results for Ising models.[15] Rather, the free energy of both phases should encounter a manifold of essential singularities at σ; although all derivatives with respect to g, T, and h should remain finite on each side of σ, neither function can be continued unambiguously to define a real metastable free energy.[3,13] The status of (4.1) as an *equation* determining $g_\sigma(T,h)$ is thus in some doubt, although as a *relation* involving $g_\sigma(T,h)$ it is certainly valid since the overall free energy $G(g,T,h)$ must be continuous everywhere including on σ.

As regards the α phase, its noncriticality and the finiteness of all its derivatives at σ, even allowing for droplets, means that we can justify an *asymptotic* expansion about the end point of the form

$$G_\alpha(g,T,h) = G_e + G_1^\alpha \Delta g + G_2^\alpha \hat{t} + G_3^\alpha h + G_4^\alpha \Delta g^2 + \cdots , \quad (4.2)$$

on and below $g_\sigma(T,h)$, where

$$\Delta g = g - g_e \quad \text{and} \quad \hat{t} = (T-T_e)/T_e . \quad (4.3)$$

However, the situation as regards the phases β, γ, and $\beta\gamma$ (or β_+ and $\vec{\beta}_-$) which are approaching criticality is more delicate. Thus it is not unreasonable to speculate that the presence of droplets of a noncritical phase in a near-critical phase might lead to a new type of criticality—say, end point criticality—with new exponents, $\alpha, \Delta, \ldots$ or, perhaps, only new amplitude ratios. Indeed, within real space renormalization groups[16,17] a critical end point is usually controlled by a fixed point Hamiltonian, say $\mathcal{H}_e^*$, with a discontinuity eigenexponent and operator, which is *distinct* from the purely critical fixed point Hamiltonian, $\mathcal{H}_c^*$, controlling behavior on the associated critical line.[2] Of course, this need *not* imply different critical behavior at the end point since $\mathcal{H}_e^*$ and $\mathcal{H}_c^*$ could have matching critical spectra: In fact, just this scenario has been observed in models yielding the Migdal-Kadanoff recursion relations![16,17] But that might not be the invariable rule. On the other hand, an $(\epsilon = 4-d)$-expansion study[2] for $n=1$ found that both critical line and end point were controlled by the same, standard $O(\epsilon)$ fixed point and so had identical critical behavior.

Previous calculations for spherical models $(n\to\infty)$ exhibiting tricritical points with associated end points also found identical criticality as on the critical line;[18] however, the critical end points examined were purely classical with no significant fluctuation contribution. For this reason we study spherical models with *non*classical end points in Parts II and III.

In fact our work also confirms the equivalence of criticality on the line and at the end point. If we accept this, generally, at least for what might be termed *regular* critical end points, the critical free energy (3.2) may be expanded in the end point vicinity by taking

$$G_0(g,t,h)=G_e+G_1^0\Delta g+G_2^0\hat{t}+G_3^0 h+G_4^0\Delta g^2+\cdots, \tag{4.4}$$

$$Q(g,t,h)=Q_e+Q_1\Delta g+Q_2\hat{t}+Q_3 h+\cdots, \tag{4.5}$$

$$U(g,t,h)=U_e+U_1\Delta g+U_2\hat{t}+U_3 h+\cdots, \tag{4.6}$$

and, for the nonlinear scaling fields

$$\tilde{t}=\hat{t}+q_1\Delta g+q_2\Delta g^2+q_3\hat{t}\Delta g+q_4\hat{t}^2+q_5h^2+\cdots, \tag{4.7}$$

$$\tilde{h}=h(1+r_1\Delta g+r_2\hat{t}+r_3h+r_4\Delta g^2+\cdots), \tag{4.8}$$

where we should note the geometrical significance of

$$q_1=-\frac{1}{T_e}\left[\frac{dT_c}{dp}\right]_e, \tag{4.9}$$

as the slope of the critical line at the end point. This follows since $\tilde{t}=0$ specifies $T_c(g)$.

Finally, equating the free energies as in (4.2), putting

$$D_i=G_i^\alpha-G_i^0 \quad \text{for } i=1,2,3,\ldots, \tag{4.10}$$

assuming that $D_1\neq 0$, and neglecting the corrections to scaling, yields

$$g_\sigma(T,h)\approx g_0(T,h)-R(T,h)|\tilde{t}|^{2-\alpha}W_\pm^0\left[\frac{U\tilde{h}}{|\tilde{t}|^\Delta}\right], \tag{4.11}$$

where the background function has the expansion

$$g_0(T,h)=g_e+g_1\hat{t}+g_2h+\cdots, \tag{4.12}$$

with $g_1=-D_2/D_1$ and $g_2=-D_3/D_1$. Thus the slope of the phase boundary and of the triple line $\{g=g_\sigma(T,0),h=0\}$, at the end point, is given by

$$g_1=T_e\left[\frac{\partial g_\sigma}{\partial T}\right]_e. \tag{4.13}$$

The smoothly varying amplitude obeys

$$R(T,h)\equiv Q[g_\sigma(T,h),T,h]/(D_1+D_2'\hat{t}+D_3'h+\cdots)$$
$$=R_e+R_1\hat{t}+R_2h+\cdots,\quad R_e=Q_e/D_1, \tag{4.14}$$

where D_2', D_3', R_1, R_2, etc., are coefficients expressible in terms of the coefficients in (4.4)–(4.8). It should also be noted that further contributions proportional to $|\tilde{t}|^{(2-\alpha)k}$ with $k=2,3,\ldots$ have been dropped and that (4.11) is not as explicit as it looks since $g_\sigma(T,h)$ enters into $\tilde{t}$ and $\tilde{h}$ via (4.7) and (4.8). Accordingly we will examine $g_\sigma(T,h)$ in more detail in various subspaces.

Before turning to this, however, let us recall a feature of the droplet approach,[13] namely that the location of the phase boundary follows by examining the free energy of one phase, say the α phase, *alone:* No direct matching of free energies is required! In fact, if one recognize that the droplets in the α phase near the end point will themselves exhibit incipient criticality, further progress can be made. The natural approach[19] is to adopt an appropriate *finite-size scaling* form[20,21] for the droplet free energies as $\tilde{t}\to 0$ on the *extended* critical line below T_e. Remarkably, the droplet picture then yields,[19] at least in leading orders, precisely the same singular behavior for the phase boundary near the end point as found here.

V. UNIVERSALITY ON SPECIAL LOCI

Let us now examine the equation for the spectator phase boundary, namely (4.11), in various regimes and define amplitudes describing the behavior of σ.

A. Coexistence surface

We specialize first to the surface $h=0$. Then when $\hat{t}\to 0\pm$ (4.11) yields

$$g_\sigma(T)-g_0(T)\approx -R_eW_\pm(0)|\hat{t}+q_1g_\sigma(T)-q_1g_e|^{2-\alpha}, \tag{5.1}$$

which, on using (4.12), is readily solved by iteration to give

$$g_\sigma(T,0)=g_e+g_1\hat{t}+\cdots-X_\pm|\hat{t}|^{2-\alpha}[1+O(|\hat{t}|^{1-\alpha})], \tag{5.2}$$

where the ellipsis denotes higher-order analytic terms. This confirms the nature of the singularity in the phase boundary mentioned in the Introduction. The amplitudes of the singular form may be written

$$X_\pm=R_e|e_0|^{2-\alpha}W_\pm(0), \tag{5.3}$$

in which it is convenient to define a geometrical factor by

$$e_{\vartheta-1}=1+\vartheta g_1q_1=1-\vartheta\left[\frac{dg_\sigma}{dT}\right]_e\left[\frac{dT_c}{\partial g}\right]_e. \tag{5.4}$$

For $\vartheta=1$ this vanishes only if the critical line λ and the triple line τ are tangent at the end point. This is clearly an anomalous situation which we will disregard by assuming henceforth that $e_0\neq 0$. Note also that for $\alpha>0$ and the configuration of phases illustrated in Fig. 1 the amplitudes $X_\pm$ are *non-negative.* By appeal to (3.9), (4.10), and (4.14) we may write the amplitudes directly in terms of observable quantities as

$$X_\pm=A_\pm(g_e)|e_0|^{2-\alpha}/(2-\alpha)(1-\alpha)(v_e-v_c), \tag{5.5}$$

where, if we take g as the pressure, v_e and v_c are just the specific volume of the spectator and critical phases, respectively, evaluated *at* the end point.[19] From this expression, which has a not unexpected similarity to a Clausius-Clapeyron relation, the actual magnitude of the $|\hat{t}|^{2-\alpha}$ singularity in $g_\sigma(T)$ or, better, in d^2g_σ/dT^2 can be estimated in realistic situations. It is also now evident that

$$X_+/X_-=A_+/A_- \tag{5.6}$$

is a *universal ratio* determined purely by bulk behavior on the critical line.

B. Small fields

For small fields above T_e the phase boundary varies analytically through $h=0$ but contains a quadratic piece diverging at T_e and given by

$$g_\sigma(T,h)-g_0(T,h)\approx -\tfrac{1}{2}Z_+h^2\hat{t}^{\,-\gamma}+O(h^4) \tag{5.7}$$

with amplitude

$$Z_+=R_eU_e^2|e_0|^{-\gamma}W_+''(0)\ . \tag{5.8}$$

About the triple line τ below T_e there is (for $n=1$ systems) a similar contribution but a term varying as $|h|$ also appears so that

$$g_\sigma(t,h)-g_0(T,h)\approx -Y|h|\,|\hat{t}|^{\beta}-\tfrac{1}{2}Z_-h^2\hat{t}^{\,-\gamma}+O(h^3), \tag{5.9}$$

where the amplitudes Y and Z_- are easily found in terms of $W_-'(0)$ and $W_-''(0)$. Reference to (3.9) and (3.10) then yields the independent universal ratios

$$Z_+/Z_-=C_+/C_- \tag{5.10}$$

and

$$\Xi_1\equiv\frac{X_+Z_+}{Y^2}=\frac{A_+C_+}{(2-\alpha)(1-\alpha)B^2}=\frac{\Theta_1}{(2-\alpha)(1-\alpha)}\ . \tag{5.11}$$

C. Field variation at criticality

Finally it is interesting to examine the intersection of the phase boundary with planes normal to σ but passing through the end point: Specifically consider the general locus given by

$$\frac{T-T_e}{g-g_e}=\vartheta\left[\frac{dT_c}{dg}\right]_e\ . \tag{5.12}$$

Note that $\vartheta=0$ corresponds to the manifold $T=T_e$ of the end point isotherm. On the other hand, $\vartheta=1$ specifies a plane which asymptotically contains the critical line, $T_c(g)$, as it approaches the end point. The phase boundary on the general locus may now be written as

$$g_\sigma(h)_\vartheta-g_e=\{g_2h-Y_c|h|^{(\delta+1)/\delta}\times[1+O(h^{(\delta-1)/\delta},h)]\}/e_{\vartheta-1}\ , \tag{5.13}$$

where the geometrical factor $e_{\vartheta-1}$ was defined above, while the amplitude

$$Y_c=R_eU_e^{(\delta+1)/\delta}W_\infty \tag{5.14}$$

must be positive for phases arranged as in Figs. 1 and 2. Finally, the related ratios

$$\Xi_2=\frac{X_+Y_c^\delta}{Y^{\delta+1}}=\frac{\Delta^\delta A_+B_c^\delta}{(2-\alpha)^{\delta+1}(1-\alpha)B^{\delta+1}}=\frac{\Delta^\delta\Theta_2}{(2-\alpha)^{\delta+1}(1-\alpha)}\ , \tag{5.15}$$

$$\Xi_3=\frac{Y^{\delta-1}Z_+}{Y_c^\delta}=\frac{\Xi_1}{\Xi_2}=\left[\frac{\delta+1}{\delta}\right]^\delta\Theta_3\ , \tag{5.16}$$

$$\Xi_4=\frac{X_+^{\delta-1}Z_+^{\delta+1}}{Y_c^{2\delta}}=\frac{\Xi_1^{\delta+1}}{\Xi_2^2}=\frac{(2-\alpha)^{\delta+1}\Theta_4}{\Delta^{2\delta}(1-\alpha)^{\delta-1}} \tag{5.17}$$

are all universal and, in principle, susceptible to observation.

D. Explicit predictions

For completeness we record the universal predictions for the phase boundary singularity amplitudes which follow from knowledge of the bulk amplitude ratios in particular cases.

1. Mean-field theory

Mean-field theory is characterized by $\alpha=0$, $\delta=3$, and $\Delta=\frac{3}{2}$ but is anomalous in that A_+ and A_- are not well defined although, of course, the specific heat exhibits a jump $\Delta\mathcal{C}$ at T_c. It is clear, however, that the Gibbsian view underlying the free-energy matching equation (4.1) is fully justified for all classical theories. Thus we conclude that $g_\sigma(T,0)$ must display a jump in curvature at T_e proportional to $\Delta\mathcal{C}$. The asymptotic equation of state for mean-field theory may be written in reduced form as

$$h=M(t+M^2)\ . \tag{5.18}$$

From this follow all the bulk universal amplitude ratios and thence we find

$$Z_+/Z_-=2 \quad\text{and}\quad \Xi_3=Y^2Z_+/Y_c^3=(\tfrac{4}{3})^3\ . \tag{5.19}$$

2. General spherical models

It is instructive to consider d-dimensional spherical models, which correspond to the $n\to\infty$ limit of n-vector models, having either short-range interactions or long-range power law couplings with $J(\mathbf{R})$ decaying as $1/R^{d+\sigma}$ $(\sigma>0)$.[8,18] Above the upper borderline dimension $d_+=\min\{4,2\sigma\}$ the leading behavior is classical; however, there are nontrivial corrections to scaling which, in turn, affect the phase boundary near an end point, as discussed in Part III. At and below $d_-=\min\{2,\sigma\}$ transitions occur for $T>0$. For $d_-<d<d_+$ criticality is always found with $\beta=\frac{1}{2}$ and

$$\gamma=1-\alpha=\Delta-\tfrac{1}{2}=\tfrac{1}{2}(\delta-1)=[(d/\sigma)-1]^{-1}>1\ . \tag{5.20}$$

The reduced asymptotic equation of state is simply

$$h=M(t+M^2)^\gamma\ . \tag{5.21}$$

Below T_c the specific heat is described by $A_-=0$ while the susceptibility, $\chi(T,h)$, diverges when $h\to 0$ so that C_- is not defined.

For an end point on a spherical model (or $n=\infty$) critical line we thence obtain the results

$$\frac{X_-}{X_+}=0,\quad \Xi_1=\frac{-1}{2(\gamma+1)},\quad \Xi_3=\left[\frac{2\gamma+2}{2\gamma+1}\right]^{2\gamma+1}\ . \tag{5.22}$$

These predictions will be tested in Part II by specific calculations for spherical models displaying nonclassical critical end points.

3. Two-dimensional Ising models

The exponents $\alpha=0(\log)$, $\delta=15$, and $\Delta=1\frac{7}{8}$ are, of course, known exactly for two-dimensional Ising models. The amplitude ratios in zero field are known exactly or to very high precision; those in a field have been estimated by series expansions.[6,22] On that basis we find

$$\frac{X_+}{X_-}=1,\quad \frac{Z_+}{Z_-}=37.69\cdots,$$
$$\Xi_1=0.159\,28\cdots,\quad \Xi_3\simeq 17.8_4\,. \tag{5.23}$$

Note, however, that in (5.2) $|\hat{t}|^{2-\alpha}$ must be replaced by $\hat{t}^{\,2}\ln|\hat{t}|$ and $|\hat{t}|^{1-\alpha}$ by $\hat{t}\ln|\hat{t}|$.

4. Three-dimensional Ising models

For three-dimensional Ising models only numerical estimates are available for exponents and amplitudes.[5,22] We may adopt[5] $\alpha\simeq 0.104$ and $\gamma\simeq 1.2395$ from which scaling gives $\Delta\simeq 1.568, \delta\simeq 4.777$. However, one must not have great confidence in the last decimal place quoted. Then we find

$$\frac{X_+}{X_-}\simeq 0.523,\quad \frac{C_+}{C_-}\simeq 4.95,\quad \Xi_1\simeq 0.32_9,\quad \Xi_3\simeq 4.3_4\,, \tag{5.24}$$

where again, the last places are uncertain.

Various simple models are known, notably the Blume-Emery-Griffiths spin-one model and the three-state Potts model in external fields, which exhibit critical end points with associated Ising critical lines. Unfortunately, none of these models seem sufficiently tractable to test the predictions (5.23) and (5.24) analytically. Numerical tests may be possible using transfer matrix methods or, perhaps, Monte Carlo calculations. It must be recognized, however, that the singularities predicted in the phase boundary $g_\sigma(T,h)$ are fairly weak in numerical terms. Most promising is the ratio $\Xi_3=Y^{\delta-1}Z_+/Y_c^\delta$ which describes the field dependence near the coexistence manifold ($h=0$).

VI. CONCLUSIONS

We have analyzed bulk thermodynamics near a critical end point with the particular aim of elucidating the singularities that may appear in the phase boundary, $g_\sigma(T,h)$, to the noncritical spectator phase. Characteristic behavior is anticipated which, it is argued, should be controlled by the universal bulk critical exponents, amplitude ratios, and scaling functions that are observable on the critical line away from the end point. Relevant bulk critical-point amplitude ratios are defined in (3.5)–(3.8) and (3.11)–(3.14). The behavior predicted for $g_\sigma(T,h)$ on particular interesting loci is then detailed in the results (5.2), (5.7), (5.9), and (5.13); the corresponding universal amplitude ratios are defined and related to the bulk ratios in (5.6), (5.10), and (5.11), and in (5.15)–(5.17). Explicit numerical predictions for these phase boundary ratios are presented for classical systems in (5.19), for general spherical models in (5.22), and for Ising models in (5.23) and (5.24).

Although our results are very plausible, they are based, as explained in Sec. III, on assumptions that are not entirely well founded inasfar as they suppose one may neglect any counter-phase or droplet fluctuations which must enter a full microscopic description near an end point. Although a droplet-picture calculation[19] corroborates our results, explicit analyses for systems actually exhibiting end points are certainly desirable and, conceivably, could lead to unanticipated modifications of the theory. Parts II and III of this paper will present such an analysis for spherical models in all dimensions and with both long- and short-range interactions.

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