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Isothermal binodal curves near a critical endpoint

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Thermodynamics in the vicinity of a critical endpoint with nonclassical exponents α, β, γ, δ, ... , is analyzed in terms of density variables (mole fractions, magnetizations, etc.). The shapes of the isothermal binodals or two-phase coexistence curves are found at and near the endpoint for symmetric and nonsymmetric situations. The spectator- (or noncritical-) phase binodal at $T=T_e$ is characterized by an exponent $(\delta+1)/\delta$ ($\simeq 1.21$) with leading corrections of relative order $1/\delta$ ($\simeq 0.21$), $\theta_4/\beta\delta$ ($\simeq 0.34$) and $1-(\beta\delta)^{-1}$ ($\simeq 0.36$); in contrast to classical (van der Waals, mean field, etc.) theory, the critical endpoint binodal is singular with a leading exponent $(1-\alpha)/\beta$ ($\simeq 2.73$) and corrections which are elucidated; the remaining, λ-line binodals also display the "renormalized exponent," $(1-\alpha)/\beta$ but with more singular corrections. [The numerical values quoted here pertain to $(d=3)$-dimensional-fluid or Ising-type systems.] *© 2001 American Institute of Physics.* [DOI: 10.1063/1.1373665]

I. INTRODUCTION AND OVERVIEW

At a critical point in a fluid (or other Ising-type or $n=1$) system two distinct phases, say, β and γ, become identical: below $T=T_c$ these two phases may coexist for appropriate values of the conjugate ordering field (or chemical potential, etc.)[1] h; above T_c they merge into a single phase, say, $\beta\gamma$. If there is some other field variable,[1] say, g, which may be varied without destroying coexistence, the critical point is drawn out into a lambda line, $T=T_c(g)$. A typical situation, which lacks any special symmetry, is shown schematically in Fig. 1. The lambda line, λ, delimits the phase boundary surface $h=h_\rho(g,T)$, labeled ρ, on which β and γ may coexist.

Now in many instances when g is varied, say, decreased, another quite distinct phase, α, will be encountered. In this case the lambda line terminates at a *critical endpoint*,[2] which is labeled E in Fig. 1. At E the phases β and γ may undergo criticality in the presence of the coexisting noncritical phase α which may be appropriately termed the *spectator phase*.[2,3] The surface bounding the spectator phase in the (g,T,h) or field space is labeled σ; on it α may coexist with phases $\beta\gamma$, β, or γ; on the triple line, τ, where the surface ρ meets the surface σ, all three phases α, β and γ may coexist.

In a previous study[2] (to be denoted **I**), we discussed the shape of the spectator-phase boundary surface, $g=g_\sigma(T,h)$, in the vicinity of the endpoint at $T=T_e$ and, by choice of origin, $h=h_e\equiv 0$. It was found that the surface is singular at E with functions such as $g_\tau(T)$, specifying the triple line, and $g_\sigma(T_e;h)$, displaying nonanalytic behavior described by a variety of critical exponents.[2,4] When, as is normally so, the lambda line is characterized by nonclassical exponents α, for the specific heat, β, for the order parameter, δ, for the critical isotherm, etc., the spectator-phase boundary exponents can all be expressed[2] in terms of α, β, and δ. Beyond that it was shown that various dimensionless ratios constructed from the amplitudes of the phase-boundary singularities should be *universal* with values also determined by the nature of the bulk criticality on the lambda line.[2,4]

These conclusions were based on a phenomenological description of the thermodynamic potentials (or Gibbs' free energies) $G^\alpha(g,T,h)$ and $G^{\beta\gamma}(g,T,h)$, for the spectator phase and for the coexisting and critical phases, respectively. The former was assumed to have a power series expansion in the vicinity of E; the latter embodied a full scaling representation of the critical line and its neighborhood.[2,4]

This formulation neglects the essential singularities expected on the σ and ρ boundaries;[5] these can, however, be discussed[4] but play only a negligible quantitative role. Our general phenomenological treatment has been checked by an extensive study of a family of spherical models which exhibit lambda lines and critical endpoints with a range of nonclassical exponents (although $\beta=\frac{1}{2}$ in all cases).[6,7]

Many experimental examples of critical endpoints are found in multicomponent fluid systems. In the simplest example, which we will particularly bear in mind, two chemical species, B and C, mix as fluids in all proportions at high temperatures forming the phase $\beta\gamma$. At lower temperatures, however, they undergo liquid–liquid phase separation, or demixing, producing phases β and γ rich in B and C, respectively. Up to a constant shift, the field h may then be taken as the chemical potential difference $\mu_B-\mu_C$. As the pressure, p, or the total chemical potential, $\mu_B+\mu_C$, either of which we may identify with the field g, is reduced, a dilute vapor phase, α, appears. Figure 1 then represents a characteristic overall phase diagram. Now in a typical experiment the tem-

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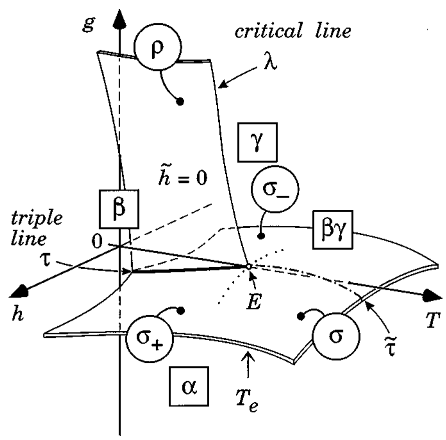

FIG. 1. The thermodynamic field space (g,T,h) exhibiting a *non*symmetric (**N**) critical endpoint, E, at the meet of a λ line, marking the edge of a phase boundary surface ρ on which phases β and γ can coexist, and a phase boundary surface σ limiting the spectator phase α. The triple line τ, on which phases α, β, and γ may coexist, extends above $T=T_e$ into the dotted-dashed line $\tilde{\tau}$ which is the intersection of σ with the extended phase boundary $\tilde{\rho}$ (not shown). Note, as discussed below, that the λ line shown here slopes downward towards the α phase as T rises, thus representing what we denote as case **A**.

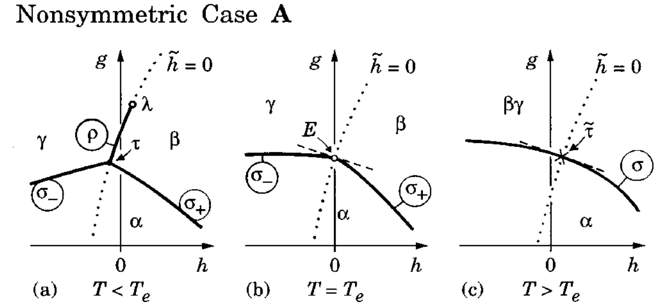

FIG. 2. Isothermal sections of an **NA** endpoint phase diagram in field space for (a) $T<T_e$, (b) $T=T_e$, and (c) $T>T_e$ corresponding schematically to the full (g,T,h) diagram shown in Fig. 1. For $T\leqslant T_e$ the phase boundary σ in Fig. 1 breaks into two pieces: σ_+ separating phases α and β, and σ_- separating α and γ. The dotted curve represents the locus $\tilde{h}(g,T,h)=0$ (see Sec. II) which coincides with the surface ρ (see Fig. 1) and defines its extension $\tilde{\rho}$ and, hence, the extended triple line $\tilde{\tau}$.

perature T is controlled and may be held fixed: corresponding to Fig. 1, the appropriate isothermal phase diagrams in the (g,h) plane then have the character shown in Fig. 2 for $T<T_e$, $T=T_e$, and $T>T_e$.

However, the chemical potentials μ_B and μ_C, or the fields h and g, are normally *not* under direct experimental control or observation; rather, the conjugate *densities*, ρ_B and ρ_C (or concentrations of B and C) or, equivalently, the densities,

$$\rho_1 = -\frac{\partial}{\partial h} G(g,T,h)|_{g,T}, \quad \rho_2 = -\frac{\partial}{\partial g} G(g,T,h)|_{T,h}, \tag{1.1}$$

are the prime experimental variables. [Note that in the example envisaged with $g=\mu_B+\mu_C$ one simply has $\rho_1 = \frac{1}{2}(\rho_B-\rho_C)$ and $\rho_2=\frac{1}{2}(\rho_B+\rho_C)$.] In the density plane (ρ_1,ρ_2) the phase boundaries ρ and σ are represented by two-phase regions bounded by smooth curves, the so-called *binodals* or *coexistence curves*; see Fig. 3. The aim of this article is to analyze in detail and generality the *shapes* of these isothermal binodal curves in the vicinity of a critical endpoint. Specifically, we will elucidate the nature of the leading and subdominant singularities that appear in the various binodals labeled $\mathcal{B}_e^{\alpha+}$, $\mathcal{B}_<^{\beta}$, etc., in Fig. 3.

It appears from Fig. 3, and detailed analysis bears it out, that the binodal curves for $T\geqslant T_e$ meet with a common tangent at the endpoints E^λ and E^α and at the extended triple points $\tilde{\tau}\alpha$ and $\tilde{\tau}\beta\gamma$ [defined by the intersection of $\tilde{\rho}$, the extended phase boundary ρ, with the surface σ in the (g,T,h) space; see **I**]. Of principal concern, then, is the way in which the binodals depart from linearity. *Above* T_e one expects analytic binodals but the behavior of the curvatures at $\tilde{\tau}\alpha$ and $\tilde{\tau}\beta\gamma$ as $T\to T_e+$ is then of interest. On the other hand, *at* $T=T_e$ one expects singular behavior at E^λ and E^α. Indeed, Borzi,[8] stimulated by Widom,[9] discussed the *non-*

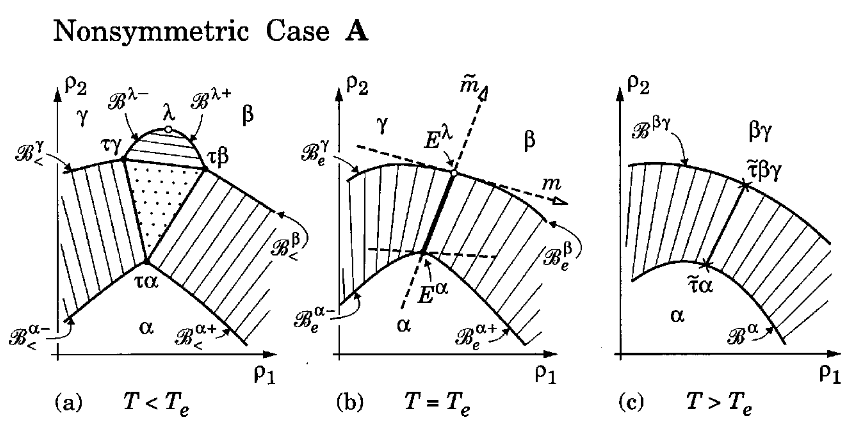

FIG. 3. Isothermal density–density (or composition) diagrams for (a) $T<T_e$, (b) $T=T_e$, and (c) $T>T_e$ for an **NA** endpoint illustrating the single-phase regions α, β, γ, and $\beta\gamma$, the two-phase regions ruled by tie-lines connecting coexisting phases, and the three-phase triangle (dotted area) in which phases corresponding to the vertices $\tau\alpha$, $\tau\beta$, and $\tau\gamma$ coexist. The various analytically distinct binodals are labeled $\mathcal{B}_<^{\alpha-}$, $\mathcal{B}_e^{\gamma}, \cdots$, where the superscript indicates the phase bounded by the binodal while the subscript serves (as needed) to specify the temperature, $T\lessgtr T_e$. The same notations apply to a symmetric **SA** endpoint. At $T=T_e$ the endpoint tieline $E^\alpha E^\lambda$ defines the $\tilde{m}$ or $m=0$ axis, shown dashed, where m and $\tilde{m}$ are fixed linear combinations of the densities ρ_1 and ρ_2 (see Sec. III); the m and $\tilde{m}$ axes on the plots (a) and (c) have been omitted for the sake of clarity but are useful to understand the motion of the various features as T passes through T_e. Note that this figure corresponds qualitatively to Figs. 1 and 2 but is *not* quantitatively accurate.

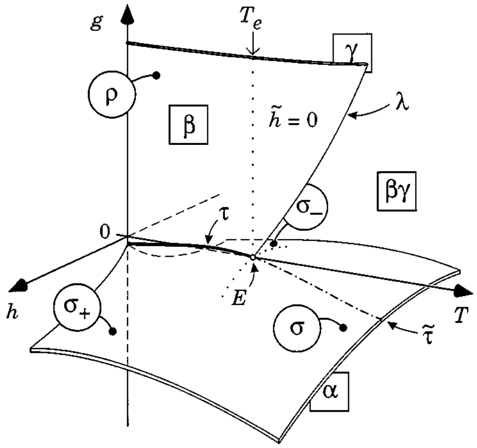

FIG. 4. Thermodynamic field space illustrating a *sym*metric critical endpoint, **SB**, for case **B** in which the λ-*line slopes upward* away from the spectator phase α as T *increases*. Beyond these differences, the phases, phase boundaries, etc., correspond precisely with those in Fig. 1.

critical binodals at the endpoint, namely, $\mathcal{B}_e^{\alpha\pm}$ in Fig. 3(b), using the simplest possible phenomenological postulate and geometrical arguments (equivalent to van der Waals and other classical theories). He concluded that the degree of tangency was controlled by a 4/3 power law (in place of a power 2 for a normal analytic tangency).

Later Klinger,[9] using a more general phenomenological classical theory, discussed the *critical* endpoint binodals, $\mathcal{B}_e^{\beta}$ and $\mathcal{B}_e^{\gamma}$ analytically; see Fig. 3(b). However, he found no evidence of singular behavior. Beyond that, Klinger confirmed the leading 4/3 power in the *non*critical or spectator binodal and found that the first correction term carries a 5/3 power.

On general grounds, however, it seems certain that the powers 4/3 and 5/3 must result from the reliance on classical theory which entails the critical exponent values $\alpha=0$, $\beta=\frac{1}{2}$, and $\delta=3$ in place of the appropriate nonclassical values $\alpha\simeq 0.10_9$, $\beta\simeq 0.32_6$, and $\delta=(2-\alpha)/\beta-1\simeq 4.8_0$ which characterize the specific heat, coexistence curve, and critical isotherm of real bulk $(d=3)$-dimensional fluids (or other systems in the Ising universality class). Indeed, Widom has conjectured[9] that in general the 4/3 power should become $(\delta+1)/\delta$. This reduces to Borzi's result when $\delta=3$ but yields an exponent value of 1.208 for real fluid systems.

Here we confirm Widom's surmise using the full scaling approach developed in **I**. Furthermore we show that Klinger's correction exponent of 5/3 is replaced, more generally, by *three* exponents, namely $(2-\alpha+\beta)/\beta\delta$, $(2-\alpha+\theta_4)/\beta\delta$, and $(3-2\alpha-\beta)/\beta\delta$. Here θ_4 is the leading correction-to-scaling exponent which has the value $\theta_4\simeq 0.54$ for $(d=3)$-dimensional Ising-type systems;[10] thus these three exponents have values of about 1.42, 1.55 and 1.57, respectively, for bulk fluids. In the classical limit attained via $d\rightarrow 4-$ one has $\theta_4\rightarrow 0$ and the second exponent reduces[11] to 4/3 while the first and third yield Klinger's value of 5/3. However, we also identify further singular exponents that must appear in the expansion of the noncritical binodal at the endpoint.

It transpires, in addition, that, contrary to Klinger's findings,[9] the critical binodal is, in general, *also singular* with a leading power $(1-\alpha)/\beta\simeq 2.7_3$ so that the binodal is much flatter at the endpoint E^{λ} than classical theory would predict. Here, and below where appropriate, we suppose $\alpha>0$ as applies to real fluids. The exponent $(1-\alpha)/\beta$ is, in fact, the same as that long known to characterize isothermal binodals passing through a lambda point (away from any endpoint); see $\mathcal{B}^{\lambda+}$ and $\mathcal{B}^{\lambda-}$ in Fig. 3(a). This behavior which is, of course, reconfirmed by our analysis reflects, in turn, the phenomenon of critical exponent renormalization.[12] The correction terms in the critical endpoint binodal are found to carry exponents $(1-\alpha+\theta_k)/\beta$ with $k=4,5,\ldots$. When one substitutes the classical values $\alpha=0$ and $\theta_k=\frac{1}{2}(k-4)$ these leading and correction exponents become 2, 3, 4, ..., which are consistent with Klinger's results and indicative of a fully analytic critical binodal.

The results sketched out here, and others for the remaining binodals shown in Fig. 3, are presented in detail in Sec. III. However, it is necessary to point out that Figs. 1–3 are special in two respects. First, as mentioned, no symmetry with respect to the ordering surface ρ has been supposed; this is quite appropriate for most fluid systems. However, as observed in **I**,[2,4] there are many other physical systems in which the thermodynamic potentials are unchanged under reflection in the *plane* ρ: one may then take $h=0$ on ρ and the symmetry becomes invariance under $h\Leftrightarrow -h$. The conceptually simplest example is an elemental ferromagnet, like nickel or iron, where $h\equiv H$ is the magnetic field and $g\equiv p$ is the pressure. Other examples are ferroelectrics, antiferromagnets, order–disorder binary alloys, and liquid helium through its transition to superfluidity;[4] however, the binodal curves are not readily accessible experimentally in some of these cases. The corresponding (g,T,h) phase space, the isothermal sections, and the binodal curves for such *symmetric critical endpoints* are illustrated in Figs. 4–6. In fact, symmetric critical endpoints are simpler in a number of respects and will be analyzed first below. Fundamentally we find that the leading singular behavior of the binodals is identical in the symmetric and nonsymmetric cases but the correction terms differ in character: see Sec. III.

A second special feature embodied in Figs. 1–3 is the *slope* of the λ line which we characterize as *negative* in the sense that if, without loss of generality, we (i) take

$$g=h=0, \quad T=T_e, \quad \text{at } E, \tag{1.2}$$

and (ii) suppose that the negative g axis lies in the α or spectator phase (see Figs. 1 and 4) then we have[2]

$$\mathbf{A}: \quad \Lambda_g \equiv T_e\left(\frac{dT_c}{dg}\right)_e^{-1}<0. \tag{1.3}$$

Conversely, as illustrated in Fig. 4, one must also consider the case of a positively sloping λ line with

$$\mathbf{B}: \quad \Lambda_g \equiv T_e\left(\frac{dT_c}{dg}\right)_e^{-1}>0. \tag{1.4}$$

As seen in Figs. 5 and 6, this produces distinct isothermal phase diagrams and new arrangements of binodal curves: note the additional notation introduced in Fig. 6.

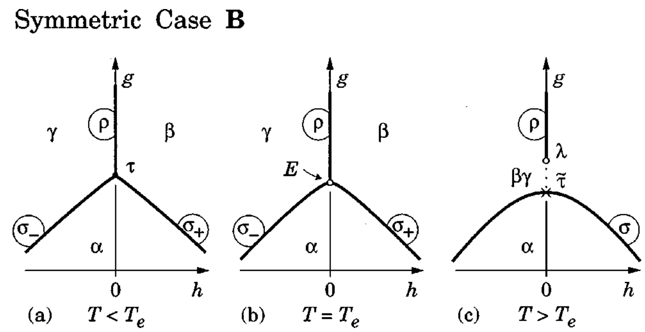

FIG. 5. Isothermal sections of an **SB** endpoint phase diagram (corresponding schematically to Fig. 4) for (a) $T<T_e$, (b) $T=T_e$, and (c) $T>T_e$. Compare with Fig. 2 and note that for $T>T_e$ the λ point and its phase boundary ρ are disconnected from the boundary σ.

One might, of course, also wish to consider the borderline cases $\Lambda_g=0$, ∞; we will not pursue these but, on the basis of our postulates for the thermodynamic potentials as set out below in Sec. II, the necessary analysis presents no further problems of principle.

In summary therefore, we will analyze the binodals for four types of critical endpoints which, using **N** for nonsymmetric and **S** for symmetric, may be labeled **NA** (Figs. 1–3) and **NB**, **SA**, and **SB** (Figs. 4–6).

In outline, the remainder of the article is as follows. Our basic scaling postulates for the thermodynamic potential $G^{\beta\gamma}(g,T,h)$ are set out in Sec. II. They are essentially the same as those introduced and discussed critically in **I** but they have been extended significantly as regards the *symmetries* of the corrections to scaling and of the nonlinear scaling fields; the notation also differs in a few details.[2] The reader prepared to take the postulates on trust[7] may proceed directly to Sec. III where the shapes of the binodals in the various cases are discussed in detail without reference to Sec. II. The analytic derivation of the results, which is straightforward in principle but a little delicate in practice, is presented in Sec. IV. Explicit formulas for the many amplitudes entering the expressions for the various binodals in Sec. III are also given in Sec. IV. In Sec. V we summarize our conclusions briefly.

II. THERMODYNAMIC POTENTIALS FOR ENDPOINTS

This section presents a complete specification of the thermodynamic potential $G(g,T,h)$ in field variables as needed for the general description of critical endpoints. It is the basis for the results described in Sec. III but need not be read to understand those results. For convenience we adopt the critical endpoint as origin for the fields g and h as specified in (1.2), and also put

$$t=(T-T_e)/T_e. \tag{2.1}$$

Thus g, t, and h measure field deviations from the endpoint E at $(g,t,h)=(0,0,0)$. (In **I** the variables g and t were denoted Δg and $\hat{t}$.) For any property $P(g,T,h)$ admitting a power series expansion about E (of indefinitely high order but not necessarily convergent) we utilize, for brevity, the semisystematic subscript notation,

$$P(g,T,h)=P_e+P_1g+P_2t+P_3h+P_4g^2+2P_5gh+2P_6gt$$
$$+2P_7ht+P_8t^2+P_9h^2+O_3(g,t,h), \tag{2.2}$$

where, here and below, $O_m(x,y,z)$ denotes a formal expansion in powers $x^jy^kz^l$ with $j+k+l\geq m$. If P is *symmetric* under $h\Leftrightarrow -h$ one has

$$P_3=P_5=P_7=0 \quad \text{(to order 3)}. \tag{2.3}$$

Functions satisfying (2.2) and (2.3) will be said to be *noncritical* (as opposed to *critical*).

Following **I** we assume that the thermodynamic potential $G^\alpha(g,T,h)$ for the spectator-phase, α, is *noncritical*. Thus one has, e.g., $G_7^\alpha=\frac{1}{2}[\partial^2G^\alpha(g,T,h)/\partial h\partial t]_e$ and, by virtue of (1.1), the endpoint densities in the spectator-phase are simply

$$\rho_1^{\alpha e}=-G_3^\alpha \quad \text{and} \quad \rho_2^{\alpha e}=-G_1^\alpha. \tag{2.4}$$

To describe the critical phases, β, γ and $\beta\gamma$, we first introduce, again following **I**, the two relevant *nonlinear* "thermal" and "ordering" scaling fields, $\tilde{t}(g,T,h)$ and $\tilde{h}(g,T,h)$, which both *vanish* on the λ line while $\tilde{h}$ also vanishes on the phase boundary ρ. For the nonlinear scaling fields we accept the noncritical expansions,[13]

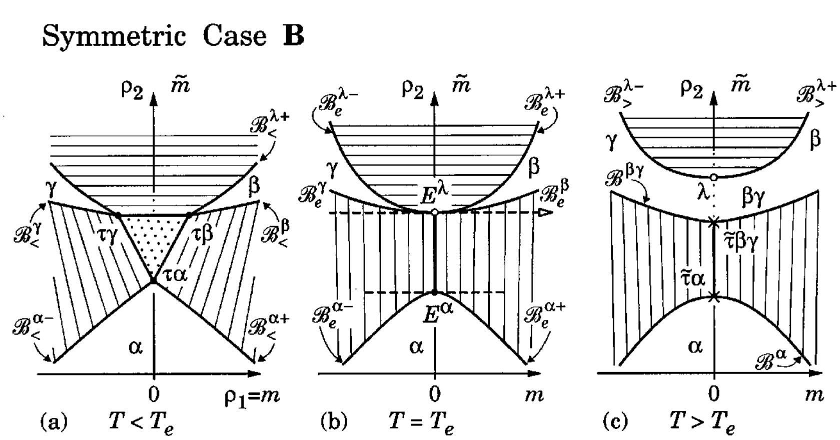

FIG. 6. Isothermal density–density diagrams for (a) $T<T_e$, (b) $T=T_e$, and (c) $T>T_e$ for an **SB** type of critical endpoint such as illustrated in Figs. 4 and 5. Compare the dispositions of the binodals with those shown in Fig. 3 and note the augmented labeling notation.

$$\tilde{t}=t+q_0h+q_1g+q_2g^2+q_3gt+q_4t^2+q_5gh+q_6h^2+q_7th+O_3(g,t,h), \quad (2.5)$$

$$\tilde{h}=h+r_{-1}t+r_0g+r_1gh+r_2th+r_3h^2+r_4g^2+r_5gt+r_6t^2+O_3(g,t,h), \quad (2.6)$$

which slightly extend those in **I** (4.7) and (4.8). It should also be mentioned at this point that *pressure-mixing* terms, which have been discovered recently in connection with the Yang–Yang anomaly in fluid systems,[14,15] are *not* considered here.[16]

In the symmetric case one has, to order 3,

$$q_0=q_5=q_7=0, \quad r_j=0, \quad \text{for} \quad j=-1,0,3\text{–}6. \quad (2.7)$$

Asymptotically, the λ line may thus be described by

$$g_\lambda(T)=\Lambda_g t+\Lambda_{g2}t^2+O(t^3),$$
$$h_\lambda(T)=\Lambda_h t+\Lambda_{h2}t^2+O(t^3), \quad (2.8)$$

where one finds

$$\Lambda_g=-\frac{1-q_0r_{-1}}{q_1-q_0r_0}, \quad \Lambda_h=\frac{r_0-q_1r_{-1}}{q_1-q_0r_0}, \quad (2.9)$$

with similar expressions for Λ_{g2}, etc. In accord with (1.3) and (1.4), we assume Λ_g does not vanish or diverge. In the symmetric case one has $\Lambda_g=-1/q_1$ and $\Lambda_h=\Lambda_{h2}=\ldots=0$, so that $\Lambda_0\equiv q_1-q_0r_0\neq 0$.

Then we need the one *relevant* scaled variable,

$$y(g,t,h)=U\tilde{h}/|\tilde{t}|^\Delta, \quad \text{with} \quad \Delta=\beta\delta=\beta+\gamma>1, \quad (2.10)$$

where the exponent relations and inequality are standard. In **I** we took $U=U(g,t,h)$ as a noncritical function; however, with no loss of generality we may take U as a *positive constant* since any dependence on g, t, and h can be absorbed into $\tilde{h}$. Beyond y we need the many *irrelevant* scaled variables,

$$y_k(g,t,h)=U_k(g,t,h)|\tilde{t}|^{\theta_k},$$
$$\theta_{k+1}\geqslant\theta_k>0, \quad k=4,5,\ldots. \quad (2.11)$$

We assume that the associated irrelevant amplitudes U_k are noncritical[13] with

$$U_k(g,t,-h)=(-)^k U_k(g,t,h) \quad \text{in case} \quad \mathbf{S}. \quad (2.12)$$

Now we can write the thermodynamic potential for the critical phase as

$$G^{\beta\gamma}(g,T,h)=G^0(g,T,h)-Q|\tilde{t}|^{2-\alpha}W_\pm(y,y_4,y_5,\cdots), \quad (2.13)$$

where the background $G^0(g,T,h)$ and the *positive* amplitude $Q(g,T,h)$ are *noncritical* while the subscript $\pm$ refers to $\tilde{t}\gtrless 0$. Physically, from the relation of α to the specific heat we have $2-\alpha>1$ but we further suppose

$$(2-\alpha)/\Delta=(\delta+1)/\delta>1, \quad (2.14)$$

as is generally valid both classically and nonclassically. For concreteness and simplicity we will, in addition, focus on $\alpha>0$ (as appropriate for bulk fluids, etc.).

We also assume, acknowledging the symmetry of the standard universality classes, that the scaling function $W_\pm(y,y_4,y_5,\cdots)$ is both universal and invariant under change of sign of the odd arguments y, y_5, y_7, $\ldots$. Beyond that we have the expansion

$$W_\pm(y,y_4,y_5,\cdots)=W^0_\pm(y)+y_4W^{(4)}_\pm(y)+y_5W^{(5)}_\pm(y)+\cdots+y_4^2W^{(4,4)}_\pm(y)+y_4y_5W^{(4,5)}_\pm(y)+\cdots,$$
$$=\sum_{\boldsymbol{\kappa}} W^{\boldsymbol{\kappa}}_\pm(y)y^{[\boldsymbol{\kappa}]}, \quad (2.15)$$

in terms of the irrelevant scaled variables y_4, $y_5,\cdots$, where for brevity we have introduced the multi-index,

$$\boldsymbol{\kappa}=0,(4),(5),\ldots,(4{,}4),(4{,}5),\ldots,(4{,}4{,}4),\ldots, \quad (2.16)$$

and the associated conventions

$$y^0\equiv 1, \quad y^{[(i,j,\ldots,n)]}\equiv y_iy_j\ldots y_n. \quad (2.17)$$

We also say $\boldsymbol{\kappa}=[(i,j,\ldots,n)]$ is *odd* or *even* according to whether the sum $i+j+\cdots+n$ is odd or even. Then with an obvious extension of notation, the symmetry of $W_\pm(y,\cdots)$ requires

$$W^{\boldsymbol{\kappa}}_\pm(-y)=(-)^{\boldsymbol{\kappa}}W^{\boldsymbol{\kappa}}_\pm(y). \quad (2.18)$$

For small y and $\tilde{t}>0$ we can then write the further expansions,

$$W^{\boldsymbol{\kappa}}_+(y)=W^{\boldsymbol{\kappa}}_{+0}+y^2W^{\boldsymbol{\kappa}}_{+2}+y^4W^{\boldsymbol{\kappa}}_{+4}+\cdots, \quad \text{for} \quad \boldsymbol{\kappa} \text{ even},$$
$$=yW^{\boldsymbol{\kappa}}_{+1}+y^3W^{\boldsymbol{\kappa}}_{+3}+y^5W^{\boldsymbol{\kappa}}_{+5}+\cdots, \quad \text{for } \boldsymbol{\kappa} \text{ odd}. \quad (2.19)$$

These series may, in general, be normalized via

$$W^0_{+2}=W^{\boldsymbol{\kappa}}_{+0}=1 \;\; (\boldsymbol{\kappa} \text{ even}) \quad \text{or} \quad W^{\boldsymbol{\kappa}}_{+1}=1 \;\; (\boldsymbol{\kappa} \text{ odd}), \quad (2.20)$$

which serve to fix the nonuniversal metrical amplitudes Q, U, $U_{k,e}$, etc.

Note, however, that in setting $W^0_{+0}=W^0_{+2}=+1$ an appeal to thermodynamic convexity,[5] together with $Q>0$ and $\alpha>0$, is entailed; see Ref. 17 where the consequences of the necessary convexity of the basic thermodynamic potentials are discussed both for the scaling functions and, more generally, for critical endpoints, thereby extending Schreinemakers' rules.[18,19]

For $\tilde{t}<0$ the existence of the first-order transition leads to $|y|$ factors in the expansions so that one has

$$W^{\boldsymbol{\kappa}}_-(y)=[W^{\boldsymbol{\kappa}}_{-0}+|y|W^{\boldsymbol{\kappa}}_{-1}+y^2W^{\boldsymbol{\kappa}}_{-2}+|y|^3W^{\boldsymbol{\kappa}}_{-3}+\cdots]\sigma_{\boldsymbol{\kappa}}(y), \quad (2.21)$$

where the special signum function is defined by

$$\sigma_{\boldsymbol{\kappa}}(y)=1 \quad \text{for} \quad \boldsymbol{\kappa} \text{ even},$$
$$=\operatorname{sgn}(y) \quad \text{for } \boldsymbol{\kappa} \text{ odd}. \quad (2.22)$$

Convexity with Q, $U>0$ then shows that W^0_{-1} and W^0_{-2} must both be *positive*; see Ref. 17.

For large arguments, $|y|\to\infty$, the individual scaling functions $W^{\boldsymbol{\kappa}}_+(y)$ and $W^{\boldsymbol{\kappa}}_-(y)$ must satisfy stringent matching conditions to ensure the analyticity of $G^{\beta\gamma}(g,T,h)$ through the surface $\tilde{t}=0$ for all $h\neq 0$. These often overlooked conditions may be written

$$W_{\pm}^{\boldsymbol{\kappa}}(y)\approx W_{\infty}^{\boldsymbol{\kappa}}|y|^{(2-\alpha+\theta[\boldsymbol{\kappa}])/\Delta}\left[1+\sum_{l=1}^{\infty} w_l^{\boldsymbol{\kappa}}(\pm|y|)^{-l/\Delta}\right]\sigma_{\boldsymbol{\kappa}}(y), \tag{2.23}$$

where the multiexponent $\theta[\boldsymbol{\kappa}]$ is defined by

$$\theta[0]\equiv 0, \quad \theta[(i,j,\cdots,n)]=\theta_i+\theta_j+\cdots+\theta_n, \tag{2.24}$$

with $i,j,\cdots,n\geqslant 4$. By virtue of the normalizations (2.20) the numerical amplitudes $W_{-j}^{\boldsymbol{\kappa}}$, $W_{+j}^{\boldsymbol{\kappa}}$, $W_{\infty}^{\boldsymbol{\kappa}}$, and $w_l^{\boldsymbol{\kappa}}$ should all be universal (as should the exponents, α, β, δ, θ_4, θ_5, ...). Beyond that, as shown in Ref. 17, convexity dictates that W_{∞}^0 and w_2^0 must be *positive* while $(w_1^0)^2/w_2^0$ must be bounded above. The *sign* of w_1^0 is not determined by convexity alone but must, in general, be *negative*: see Ref. 17. This plays an important role in determining allowable density diagrams.

Finally, from (2.13) we note that the critical endpoint densities are

$$\rho_1^{\lambda e}=-G_3^0, \quad \rho_2^{\lambda e}=-G_1^0; \tag{2.25}$$

see Fig. 3(b).

To close this section we recall from **I** that the phase boundary σ or $g=g_\sigma(T,h)$ follows by equating the two expressions $G=G^{\alpha}(g,T,h)$ and $G=G^{\beta\gamma}(g,T,h)$. Consequently, it is useful to define the thermodynamic potential difference,

$$D(g,T,h)=G^{\alpha}(g,T,h)-G^0(g,T,h), \tag{2.26}$$

which is noncritical by virtue of the definition of G^0 in (2.13). By our conventions the negative g axis, i.e., $t=h=0$, $g<0$, lies in the α phase (see Figs. 1 and 4); this implies $D_1>0$. The phase boundary ρ and its extension $\tilde{\rho}$ above $T_c(g)$ is given by $\tilde{h}(g,T,h)=0$. As in **I**(5.4), we will assume that the λ line is *not tangent* to the triple line τ at E. The densities ρ_1 and ρ_2 on the boundaries σ and ρ then follow from (1.1) and, by eliminating g and h at fixed T, the various isothermal binodals can be computed as expansions about E or about λ; see Figs. 3 and 6. We postpone the details until Sec. IV and turn next to describing the results.

III. ENDPOINT BINODALS AND THEIR INTERRELATIONS

We now describe the results of our analysis of the possible shapes of the various binodal curves and their interrelations with one another as illustrated in Figs. 3 and 6. After some preliminaries describing the "rectification" of the binodals, we consider first the behavior near the λ line: this entails only the free energy $G^{\beta\gamma}(g,T,h)$ and, inasfar as the corrections to scaling are involved, extends previous knowledge somewhat. Then the binodals at the critical endpoint temperature $T=T_e$ are described; these are, perhaps, of most interest. The binodals associated with the σ surface above T_e are discussed next. These are analytic but their slopes and curvatures display critical singularities as $T\to T_e+$. Finally, the binodals associated with the three-phase triangle below T_e are considered.

A. Rectification of the binodals

We approach the description of the binodal curves by supposing that at fixed T one may observe the densities (ρ_1,ρ_2) of various pairs of coexisting phases. In *binary fluid* mixtures ρ_1 and ρ_2 might correspond directly to the number densities of the two species, B and C. In *ternary mixtures*, however, observations would normally be conducted at fixed temperature and pressure and varying composition. Then ρ_1 and ρ_2 would each represent convenient *linear combinations* of the number densities of the three species, say, A, B, and C as represented typically in a triangle diagram. [Our analysis also applies to observations of *quaternary* mixtures *if sections* of the thermodynamic space corresponding to constant temperature, pressure, *and* a third field (or combination of chemical potentials) are constructed; however, experiments are not normally conducted that way and some further analysis would be needed to describe, say, a section at constant T, p, and ρ_3.]

We suppose next that the critical endpoint temperature T_e itself can be determined with reasonable precision so that the variable $t=(T-T_e)/T_e$ of (2.1) is well defined. Then the densities $(\rho_1^{\alpha e},\rho_2^{\alpha e})\equiv E^{\alpha}$ and $(\rho_1^{\lambda e},\rho_2^{\lambda e})\equiv E^{\lambda}$ of the spectator and critical phases *at* the endpoint can be found; see Figs. 3(b) and 6(b). These define an axis of slope,

$$L_\sigma\equiv\Delta\rho_1/\Delta\rho_2=(\rho_1^{\lambda e}-\rho_1^{\alpha e})/(\rho_2^{\lambda e}-\rho_2^{\alpha e}). \tag{3.1}$$

A natural second axis is found by noting that according to classical theory[9] the critical binodals $\mathcal{B}_e^{\beta}$ and $\mathcal{B}_e^{\gamma}$ have a well defined common tangent at E^{λ} of slope $(d\rho_1/d\rho_2)_{\mathcal{B}_e^{\beta}}^{e}\equiv 1/L_\rho$, say. This is confirmed by our more general analyses which, indeed, predict that the binodals are flatter at E^{λ} which eases the practical determination of L_ρ. (Note that it proves convenient to define L_ρ reciprocally with respect to L_σ: see below.[20])

To describe the various binodals near the endpoint it is then natural to adopt new density variables, m and $\tilde{m}$, which are linearly related to ρ_1 and ρ_2 but utilize E^{λ} as the origin and are oriented along the axes just specified: see Figs. 3(b) and 6(b). Henceforth, therefore, we will utilize the *rectified density variables*,

$$m=\rho_1-\rho_1^{\lambda e}-L_\sigma(\rho_2-\rho_2^{\lambda e}), \tag{3.2}$$

$$\tilde{m}=\rho_2-\rho_2^{\lambda e}-L_\rho(\rho_1-\rho_1^{\lambda e}). \tag{3.3}$$

Furthermore, without loss of generality[20] we assume that *the only pure phase located within the quadrant* $m>0$, $\tilde{m}>0$, *at* $T=T_e$ *is the* β *phase*. Then, as illustrated in Figs. 3(b) and 6(b), the α phase at $T=T_e$ is restricted to $\tilde{m}<0$ and only the γ phase lies in the quadrant $m<0$, $\tilde{m}>0$.

The notations m and $\tilde{m}$ are suggested by the magnetic case in which m, the magnetization, is the primary order parameter discontinuous across ρ that couples to the ordering field h, while $\tilde{m}$ is a secondary or subdominant order parameter conjugate to g. Note that for *symmetric endpoints* we have[20] $L_\sigma=L_\rho=0$ so that if one shifts the definitions of the densities in a natural way to yield an origin $\rho_1^{\lambda e}=\rho_2^{\lambda e}=0$ one simply has $m=\rho_1$ and $\tilde{m}=\rho_2$: see Fig. 6.

B. Lambda line and associated binodals

We note first (that within the postulates of Sec. II) the densities on the λ line are *noncritical* functions of T so that we have

$$m_\lambda(T)=M_1t+M_2t^2+\cdots, \tag{3.4}$$

$$\tilde{m}_\lambda(T)=\tilde{M}_1t+\tilde{M}_2t^2+\cdots. \tag{3.5}$$

For a symmetric endpoint all the M_j vanish identically. Beyond that, the coefficients M_j and $\tilde{M}_j$ are not restricted in magnitude or sign although, of course, the λ line itself cannot extend beyond the endpoint. Thus one must, here, have $t\leqslant 0$ in case **A** and $t\geqslant 0$ in case **B**.

Next notice that the binodals $\mathcal{B}_<^{\lambda\pm}$ for $T<T_e$ (see Fig. 6) $\mathcal{B}_e^{\lambda\pm}$ for $T=T_e$, and $\mathcal{B}_>^{\lambda\pm}$ for $T>T_e$ can all be treated together since by our postulates all of these binodals depend only on the free energy of the critical phase. Furthermore, inasfar as they are not truncated by the spectator phase, they must all share the same singularities and vary uniformly with T. It is also convenient to describe the binodals with the aid of a parameter $s\geqslant 0$ (related to $|\tilde{t}|^\beta$) which vanishes on the λ line and increases into the β and γ phases: coexisting phases correspond to the same value of s.

In the *symmetric case*, **S**, the binodals associated with the λ line or ρ boundary may then be specified by

$$m_\pm=\pm Bs[1+b_4s^{\theta_4/\beta}+b_1s^{1/\beta}+b_{1,4}s^{(1+\theta_4)/\beta}+\cdots+b_5s^{\delta+(\theta_5/\beta)}+\cdots], \tag{3.6}$$

$$\tilde{m}=\tilde{m}_\lambda(T)+\tilde{A}s^{(1-\alpha)/\beta}[1+\tilde{a}_4s^{\theta_4/\beta}+\tilde{a}_1s^{1/\beta}+\cdots+\tilde{a}_{\mathbf{n}}s^{\tilde{\zeta}(\mathbf{n})}+\cdots]+\tilde{K}s^{1/\beta}[1+k_1s^{1/\beta}+\cdots+k_ls^{l/\beta}+\cdots]. \tag{3.7}$$

In (3.6) the general correction term has the form $b_{\mathbf{n}}(t)s^{\zeta(\mathbf{n})}$ where $\mathbf{n}=[n_k]$ is a multi-index with $n_k\geqslant 0$ and the exponents here and in (3.7) have the form

$$\beta\tilde{\zeta}(\mathbf{n})=n_0+\sum_{j\geqslant 2}n_{2j}\theta_{2j}, \tag{3.8}$$

$$\beta\zeta(\mathbf{n})=n_0+\sum_{j\geqslant 2}[n_{2j}\theta_{2j}+n_{2j+1}(\Delta+\theta_{2j+1})]. \tag{3.9}$$

The appearance of the exponent $\Delta=\beta\delta$ is due to the symmetry which acts to suppress the odd irrelevant variables.

The correction amplitudes $\tilde{a}_4(t)$, $\tilde{a}_1(t),\ldots$, $b_4(t),\ldots$, are noncritical but, generally, of indeterminate sign. However, the noncritical amplitude $B(t)=B_e+B_2t+\cdots$ is positive with our conventions and the signs $\pm$ correspond to the β and γ phases, respectively. The amplitudes $\tilde{A}(t)=\tilde{A}_e+\tilde{A}_2t+\cdots$ and $\tilde{K}(t)=\tilde{K}_e+\tilde{K}_2t+\cdots$ are also noncritical. For $\alpha>0$, as we may assume here, the amplitude $\tilde{A}$ must be negative in case **A** while it is positive in case **B**. For $\alpha<0$ the amplitude $\tilde{K}$ would have to have matching signs but that is not demanded for $\alpha>0$. Explicit expressions for $\tilde{A}_e$, B_e, etc. are given in (4.26) and (4.27).

It is clear by symmetry that the $(m,\tilde{m})$ *tielines* connecting coexisting phase points are all "horizontal," that is, parallel to the m axis ($\tilde{m}=0$); see Fig. 6. Similarly, the *diameter* of the ρ binodals, defined as the locus of midpoints of the tielines, is given simply by $m_{\text{diam}}=0$, $\tilde{m}_{\text{diam}}\geqslant\tilde{m}_\lambda(T)\geqslant 0$.

The *symmetric* λ *binodals* may finally be expressed directly in terms of m as a variable by solving (3.6) for s and substituting in (3.7). With $x=|m/B|$ this yields

$$\tilde{m}=\tilde{m}_\lambda(T)+\tilde{A}x^{(1-\alpha)/\beta}[1+\overline{a_4}x^{\theta_4/\beta}+\overline{a_1}x^{1/\beta}+\cdots]+\tilde{K}x^{1/\beta}[1+\overline{k_4}x^{\theta_4/\beta}+\overline{k_1}x^{1/\beta}+\cdots], \tag{3.10}$$

where $\overline{a_4}=\tilde{a}_4-(1-\alpha)b_4/\beta$ and so on. The term in $\tilde{A}$ provides the dominant behavior (when $\alpha>0$) with $(1-\alpha)/\beta\simeq 2.73$ for Ising $d=3$ quoted in the Introduction. However, the term in $\tilde{K}$ provides strongly competing corrections of relative order $|m|^{\alpha/\beta}$: note that $1/\beta\simeq 3.07$. The higher order correction terms run through all powers of x with exponents of the form $\zeta(\mathbf{n}_1)+\zeta(\mathbf{n}_2)+\cdots+\zeta(\mathbf{n}_l)$.

The *nonsymmetric*, **N**, binodals associated with the λ line or ρ surface [see Fig. 3(a)] may be described similarly. In terms of the parameter s we find

$$\begin{aligned}m_\pm=m_\lambda(T)&\pm Bs[1+b_4s^{\theta_4/\beta}+b_1s^{1/\beta}+\cdots\pm b_5s^{\theta_5/\beta}\pm\cdots]\\&+As^{(1-\alpha)/\beta}[1+a_4s^{\theta_4/\beta}+a_1s^{1/\beta}+\cdots\pm a_5s^{\theta_5/\beta}+\cdots]\\&+Ks^{1/\beta}[1+\cdots+k_ls^{l/\beta}+\cdots],\end{aligned} \tag{3.11}$$

$$\begin{aligned}\tilde{m}_\pm=\tilde{m}_\lambda(T)&+\tilde{A}s^{(1-\alpha)/\beta}[1+\tilde{a}_4s^{\theta_4/\beta}+\tilde{a}_1s^{1/\beta}+\cdots\\&\pm\tilde{a}_5s^{\theta_5/\beta}\pm\cdots]+\tilde{K}s^{1/\beta}[1+\cdots+\tilde{k}_ls^{l/\beta}+\cdots]\\&\pm\tilde{B}s^{(1+\beta)/\beta}[1+\tilde{b}_4s^{\theta_4/\beta}+\cdots\pm\tilde{b}_5s^{\theta_5/\beta}\pm\cdots]\\&\pm B'ts[1+b_4's^{\theta_4/\beta}+\cdots\pm b_5's^{\theta_5/\beta}\pm\cdots],\end{aligned} \tag{3.12}$$

where, again, all the coefficients are noncritical and the same remarks as before apply to the signs of $\tilde{A}$, $\tilde{K}$, and B. The correction factors for the A, $\tilde{A}$, B, $\tilde{B}$, and B' terms run through all powers of s with exponents of the form $(n_0+\theta[\boldsymbol{\kappa}])/\beta$ [recalling the definitions (2.16), (2.24), etc.]; terms with odd $\boldsymbol{\kappa}$ carry $\pm$ signs; when $n_0=0$ we have $\tilde{a}_{\boldsymbol{\kappa}}=a_{\boldsymbol{\kappa}}$, and $\tilde{b}_{\boldsymbol{\kappa}}=b_{\boldsymbol{\kappa}}$. Expressions for A, $\tilde{A}$, etc., are given in (4.28)–(4.31).

Now note that the amplitude B' carries a factor t which vanishes at T_e. Away from the endpoint this term induces a linear variation of $\tilde{m}$ with m which simply means that the tangents to the binodals at the λ point (for $T\neq T_e$) are no longer parallel to the tangent at the endpoint. Such a variation is, of course, to be expected and does not represent any real change of shape as T deviates from T_e. To see this more explicitly, note that we may redefine the coefficient L_ρ, which enters the definition (3.3) of $\tilde{m}$, as a noncritical function, $L_\rho(t)$, chosen so that the tangent at the λ point is always parallel to $\tilde{m}=0$ (i.e., to the m axis); then one has $B'\equiv 0$ while the other terms in (3.12) do not change form. With this understanding for $t\neq 0$ we may conveniently define

$$\Delta m=m-m_\lambda(t),\quad \Delta\tilde{m}=\tilde{m}-\tilde{m}_\lambda(t), \tag{3.13}$$

which reduce to m and $\tilde{m}$, respectively, at the endpoint.

The *diameters* of the nonsymmetric λ binodals may now be found parametrically by multiplying out in (3.11) and (3.12) and dropping all terms which carry ± signs. If the parameter s is eliminated in favor of $\tilde{x}=\Delta\tilde{m}_{\mathrm{diam}}/\tilde{A}$, the diameters can be written

$$\Delta m_{\mathrm{diam}}=A\tilde{x}\,[1+\mathcal{K}_\lambda\tilde{x}^{\alpha/(1-\alpha)}+\cdots+a_4\tilde{x}^{\theta_4/(1-\alpha)}+\cdots]+\mathcal{U}_\lambda\tilde{x}^{(\beta+\theta_5)/(1-\alpha)}[1+\cdots], \tag{3.14}$$

where we suppose $\alpha>0$ while

$$\mathcal{K}_\lambda=(\tilde{A}K-A\tilde{K})/\tilde{A}A \quad \text{and} \quad \mathcal{U}_\lambda=Bb_5. \tag{3.15}$$

We see that the slope $(\partial m/\partial\tilde{m})$ of the diameter remains finite at the endpoint but, in general, the curvature *diverges* at the endpoint.

The slopes $\Sigma_\lambda=\Delta\tilde{m}/\Delta m$ of the tielines follow similarly from the terms in (3.11) and (3.12) carrying the ± signs. Using, again, $\tilde{x}=\Delta\tilde{m}_{\mathrm{diam}}/\tilde{A}$ as the variable one finds, for $\alpha>0$,

$$\Sigma_\lambda=\frac{\tilde{B}}{B}\tilde{x}^{1/(1-\alpha)}\left[1-\frac{\tilde{K}}{(1-\alpha)\tilde{A}}\tilde{x}^{\alpha/(1-\alpha)}+(\tilde{b}_4-b_4)\tilde{x}^{\theta_4/(1-\alpha)}+\cdots+\frac{\tilde{A}}{\tilde{B}}\tilde{x}^{(\theta_5+\Delta-2)/(1-\alpha)}+\cdots\right]. \tag{3.16}$$

As was anticipated, the tielines do not, in general, remain parallel to the λ-point binodal tangent; however, the variation in slope is evidently *slower* than linear in $\Delta\tilde{m}$.

Finally, one may eliminate s between (3.11) and (3.12) directly and write the general, *nonsymmetric* λ *binodals* in terms of $x=|\Delta m/B|$ as

$$\Delta\tilde{m}=\tilde{A}x^{(1-\alpha)/\beta}[1\pm a_B\tilde{B}x^{(\alpha+\beta)/\beta}+\overline{a}_4x^{\theta_4/\beta}\pm a_AAx^{(\Delta-1)/\beta}\pm a_KKx^{(1-\beta)/\beta}+\cdots\pm\overline{a}_5x^{\theta_5/\beta}+\cdots]+\tilde{K}x^{1/\beta}[1+\overline{b}_4x^{\theta_4/\beta}\pm\overline{b}_AAx^{(\Delta-1)/\beta}\pm\overline{b}_KKx^{(1-\beta)/\beta}+\cdots], \tag{3.17}$$

where the ± signs refer to $\Delta m \gtrless 0$ (for $B>0$) while

$$a_A=a_K=-(1-\alpha)/\beta B, \quad a_B=1/\tilde{A}, \qquad \overline{a}_4=\tilde{a}_4-(1-\alpha)b_4/\beta, \quad \overline{b}_4=-b_4/\beta,\ \ldots. \tag{3.18}$$

We see that the leading behavior of the binodals, with exponent $(1-\alpha)/\beta$ (for $\alpha>0$), is the same as in the symmetric case (3.10). The surprising new feature, however, is the large number of numerically similar low-order correction terms. If we write the expansion for a general binodal in the form

$$\Delta\tilde{m}=\sum_i \mathcal{A}_i^\pm|m|^{\psi_i} \tag{3.19}$$

(with ± for $m\gtrless 0$), the nonsymmetric λ-line binodals generate the exponent sequence

$$\psi_i^\lambda\beta=1-\alpha,\ 1,\ 1+\beta,\ 1-\alpha+\theta_4,\ 2-2\alpha-\beta,\ 1+\theta_4,\ 2-\alpha-\beta,\ 2-\beta,\ \cdots,\ 1-\alpha+\theta_5,\ \cdots. \tag{3.20}$$

For $d=3$ the Ising numerical values are

$$\psi_i^\lambda\beta\simeq 0.89_1,\ 1,\ 1.32_6,\ 1.43,\ 1.46,\ 1.54,\ 1.57,\ 1.67,\ \ldots,\ 1.9,\ \ldots, \tag{3.21}$$

where, here and below, we use the *rough* approximation $\theta_5\simeq 1.0$; when $d\to 4-$ one gets 1, 1, $\frac{3}{2}$, 1, $\frac{3}{2}$, 1, $\frac{3}{2}$, $\frac{3}{2}$, $\cdots$, $\frac{3}{2}$, $\cdots$, . Finally, note that the presence of the various ± signs in (3.17) reflects the nontrivial behavior of the diameter and consequent lack of binodal symmetry outside the innermost asymptotic region.

C. Spectator phase boundary at the endpoint

The spectator phase, α, is bounded in the space of thermodynamic fields by the surface σ (see Figs. 1 and 4) which may be specified by the function $g_\sigma(t,h)$ which, as explained in **I**, is found by equating the α and $\beta\gamma$ free energies, i.e., by solving $G^\alpha(g_\sigma,t,h)=G^{\beta\gamma}(g_\sigma,t,h)$. In leading order this was carried out in **I** but, for the present purposes, it is useful to have the results correct to higher order. Here we present expressions for $T=T_e$ (or $t=0$), i.e., on the endpoint isotherm.

A detailed analysis is presented in Sec. IV C where one sees that it is advantageous to retain $\tilde{h}$ as a principal variable. The results for the *symmetric case* are the simplest in form: we find

$$g_\sigma(t=0;\tilde{h})=-J|\tilde{h}|^{(\delta+1)/\delta}Z_S(|\tilde{h}|)-J_2\tilde{h}^2-J_4|\tilde{h}|^{2+(2/\delta)}+\cdots, \tag{3.22}$$

where the singular correction factor is

$$Z_S(z)=1\pm c_1z^{(1-\alpha)/\Delta}+c_2z^{2(1-\alpha)/\Delta}+c_3z^{2-(1/\Delta)}+c_4z^{\theta_4/\Delta}\pm c_4'z^{(1-\alpha+\theta_4)/\Delta}+c_5z^{1+(\theta_5/\Delta)}+\cdots. \tag{3.23}$$

The *upper* (plus) signs in Z_S correspond to case **B** or $q_1<0$; recall (1.4) and Fig. 4; the *lower* (minus) signs describe case **A** when $q_1>0$; see (1.3) and Fig. 1.

The leading amplitude in (3.22) is given, using (2.26), by

$$J=Q_eU^{(\delta+1)/\delta}W_\infty^0/(D_1-r_0D_3), \tag{3.24}$$

where Q_e and U are defined via (2.13) and (2.10) while, for the symmetric case, one has $r_0D_3=0$ and $J>0$. In addition we state

$$c_1=w_1^0|q_1|J/U^{1/\Delta}, \quad c_2=w_2^0q_1^2J^2/U^{2/\Delta}, \tag{3.25}$$

while the other coefficients are recorded in Sec. IV C. The result (3.22) can be expressed in terms of h by using

$$\tilde{h}=h[1-r_1J|h|^{(2-\alpha)/\Delta}\mp r_1c_1J|h|^{(3-2\alpha)/\Delta}+\cdots], \tag{3.26}$$

which, however, is valid *only* for $t=0$ and $g=g_\sigma$. We note that $(\delta+1)/\delta=(2-\alpha)/\Delta\simeq 1.21$ is in agreement with **I**; see also Fig. 5 for a portrayal of $g_\sigma(0,h)$. We defer discussion of the correction exponents until the noncritical/spectator binodals are presented; see Eqs. (3.36) and (3.44).

In the *nonsymmetric case* the leading variation of $g_\sigma(t=0)$ is, in general, *linear* in $\tilde{h}$ (and h): see Fig. 2. Specifically, subject to

$$J_1 \equiv D_3/(D_1 - r_0 D_3) \neq 0, \ \infty, \tag{3.27}$$

we find

$$g_\sigma(t=0;\tilde{h}) = -J_1\tilde{h} - J|\tilde{h}|^{(\delta+1)/\delta} Z_N(|\tilde{h}|) - J_2\tilde{h}^2 - J_3\tilde{h}|\tilde{h}|^{(\delta+1)/\delta} - J_4|\tilde{h}|^{2(\delta+1)/\delta} + \cdots, \tag{3.28}$$

where the *non*symmetric singular factor has the expansion

$$\begin{aligned} Z_N(z) = {}& 1 + \tilde{\sigma}_t d_1 z^{1-(1/\Delta)} - d_1' z^{(1-\alpha)/\Delta} + d_2 z^{2-(2/\Delta)} \\ & - (\tilde{\sigma}_t d_1 d_1' + \tilde{\sigma}_h d_2') z^{(\Delta-\alpha)/\Delta} + (d_2'' + d_1'^2) z^{2(1-\alpha)/\Delta} \\ & + \tilde{\sigma}_t d_3 z^{3-(3/\Delta)} - (d_3' + \tilde{\sigma}_t d_3'') z^{2-(1+\alpha)/\Delta} + d_3''' z^{2-(1/\Delta)} \\ & + d_4 z^{\theta_4/\Delta} + \tilde{\sigma}_t d_4' z^{(\theta_4+\Delta-1)/\Delta} - (d_4'' + d_1' d_4) \\ & \times z^{(\theta_4+1-\alpha)/\Delta} + \tilde{\sigma}_h d_5 z^{\theta_5/\Delta} + \tilde{\sigma}_t \tilde{\sigma}_h d_5' z^{(\theta_5+\Delta-1)/\Delta} \\ & - \tilde{\sigma}_h (d_5'' + d_1' d_5) z^{(\theta_5+1-\alpha)/\Delta} - \cdots . \end{aligned} \tag{3.29}$$

The two signum factors are given by

$$\tilde{\sigma}_t = \mathrm{sgn}(\tilde{t}) = \mathrm{sgn}(\tilde{q}h), \quad \tilde{\sigma}_h = \mathrm{sgn}(\tilde{h}) = \mathrm{sgn}(j_1 h), \tag{3.30}$$

in which we suppose the coefficients

$$\tilde{q} = q_0 - q_1(D_3/D_1), \quad j_1 = 1 - r_0(D_3/D_1), \tag{3.31}$$

are nonvanishing; this will be true in the general nonsymmetric case. (We do not analyze the exceptions although no problems of principle arise.)

We see from (3.28)–(3.30) that terms which change sign are not now determined simply by the slope of the λ line (case **A** or case **B**), as in the symmetric situation, but rather by more complicated considerations. This arises simply because the manifold $\tilde{t}=0$ in the (g,t,h) space (see Fig. 1) can cut the plane $t=0$ in various ways. For small asymmetry, j_1 remains positive giving $\tilde{\sigma}_h = \mathrm{sgn}(h)$ but $\tilde{q}$ may be of either sign. As expected from **I**, the leading singularity in g_σ is the same as in the symmetric situation; however, the corrections now contain further, new powers.

The leading correction amplitudes in Z_N are

$$\begin{aligned} d_1 &= w_1^0 |\tilde{q}|/|j_1| U^{1/\Delta}, \\ d_1' &= w_1^0 (q_1 - q_0 r_0) J/U^{1/\Delta}. \end{aligned} \tag{3.32}$$

The remaining leading coefficients are listed in Sec. IV C. As before the result (3.28) can be expressed in terms of h by making the substitution,

$$\tilde{h} = j_1 h - j|h|^{(\delta+1)/\delta} + j' h|h|^{2/\delta} - \tilde{\sigma}_t j''|h|^{(3-2\alpha-\beta)/\Delta} - j_2 h^2 + \cdots, \tag{3.33}$$

where $j = r_0 J j_1 |j_1|^{(\delta+1)/\delta}$ while j', etc. are given below in (4.48).

D. Noncritical endpoint binodals

We are now in a position to answer Widom's question regarding the shape of the noncritical or spectator-phase binodals, $\mathcal{B}_e^{\alpha\pm}$, *at* the endpoint. The essential point is that the densities ρ_1 and ρ_2 and, hence, m and $\tilde{m}$, are *noncritical* functions of g, t, and h in the spectator-phase α since $G^\alpha(g,t,h)$ is noncritical. Consequently, on the endpoint isotherm, $t=0$, the singular shape of the α binodals directly reflects the singular shape of the phase boundary $g_\sigma(0,h)$.

To state the results for the *symmetric case* we introduce the endpoint susceptibilities,

$$\chi_e^\alpha = -2G_9^\alpha > 0, \quad \tilde{\chi}_e^\alpha = -2G_4^\alpha > 0, \tag{3.34}$$

and the endpoint density

$$\tilde{m}_e^\alpha = -G_1^\alpha + G_1^0 < 0. \tag{3.35}$$

The noncritical binodal is then given by

$$\tilde{m} = \tilde{m}_e^\alpha - C|x_\alpha|^{(\delta+1)/\delta} Z_S(|x_\alpha|) - C_2 x_\alpha^2 - C_3 x_\alpha^{2(\delta+1)/\delta} + \cdots, \tag{3.36}$$

where

$$\begin{aligned} x_\alpha &= m/\chi_e^\alpha, \quad C = J\tilde{\chi}_e^\alpha, \\ C_2 &= D_9 \tilde{\chi}_e^\alpha / D_1, \quad C_3 = \left(\frac{D_4}{D_1} - \frac{Q_1}{Q_e}\right) J^2 \tilde{\chi}_e^\alpha, \end{aligned} \tag{3.37}$$

while $Z_S(z)$ is given in (3.23). The leading exponent is $(\delta+1)/\delta = (2-\alpha)/\Delta$ as stated in the Introduction. If we use the general binodal expansion (3.19) the sequence of exponents arising now is

$$\begin{aligned} \psi_i^\alpha \Delta = {}& 2-\alpha, \ 2-\alpha+\theta_4, \ 3-2\alpha, \ 4-2\alpha-2\beta, \\ & 3-2\alpha+\theta_4, \ 4-3\alpha, \ 5-3\alpha-2\beta, \ldots, \\ & 4-2\alpha-\beta+\theta_5, \ldots, \quad (\mathbf{S}), \end{aligned} \tag{3.38}$$

with Ising $d=3$ values

$$\psi_i^\alpha \simeq 1.20_8, \ 1.55, \ 1.78, \ 2, \ 2.12, \ 2.35, \ 2.57, \ldots, \ 2.9, \ldots, \quad (\mathbf{S}) \tag{3.39}$$

(using, again, $\theta_5 \simeq 1.0$).

In the limit $d \to 4-$ the sequence for ψ_i^α is $\frac{4}{3}$, $\frac{4}{3}$, 2, 2, 2, $\frac{8}{3}$, $\frac{8}{3}$, ..., $\frac{8}{3}$, ... Note that the leading correction exponent found by Klinger[9] was $\frac{5}{3}$. His classical phenomenological treatment should correspond to $d \to 4-$ but $\frac{5}{3}$ does *not* appear here: the reason is that he did not (expressly) consider the symmetric situation. We also find the exponent $\frac{5}{3}$ (and others) when symmetry is lacking.

In the *nonsymmetric* case, the endpoint susceptibilities become more complicated; we find they are given by

$$\chi_e^\alpha = -2(G_9^\alpha - 2L_\sigma G_5^\alpha + L_\sigma^2 G_4^\alpha) > 0, \tag{3.40}$$

$$\tilde{\chi}_e^\alpha = -2(G_4^\alpha - 2r_0 G_5^\alpha + r_0^2 G_9^\alpha) > 0, \tag{3.41}$$

where the significance of the axis slope, L_σ, was explained in Sec. III A above. From (3.1), (2.4) and (2.25) we obtain

$$L_\sigma = (G_3^\alpha - G_3^0)/(G_1^\alpha - G_1^0), \tag{3.42}$$

while the endpoint density is

$$\tilde{m}_e^\alpha = r_0(G_3^\alpha - G_3^0) - G_1^\alpha + G_1^0 < 0. \tag{3.43}$$

Using, again, $x_\alpha = m^\alpha/\chi_e^\alpha$ as a variable, the noncritical endpoint binodal in the *nonsymmetric* case is expressed by

$$\tilde{m}^\alpha = \tilde{m}_e^\alpha + \tilde{m}_1^\alpha x_\alpha + \tilde{m}_2^\alpha |x_\alpha|^{(\delta+1)/\delta} \pm \tilde{m}_3^\alpha |x_\alpha|^{(\delta+2)/\delta} + \cdots, \tag{3.44}$$

where $\pm$ corresponds to $h \gtrless 0$ while the amplitudes $\tilde{m}_1^\alpha$, $\tilde{m}_2^\alpha, \ldots$, are presented below. The linear variation of $\tilde{m}^\alpha$ with x_α shows that the tangent to the noncritical endpoint binodal at the endpoint E^α is, in general, *not* parallel to the tangent at E^λ (the m axis): see Fig. 3(b). The corresponding amplitude, $\tilde{m}_1^\alpha$, is

$$\tilde{m}_1^\alpha = 2(-G_5^\alpha + r_0 G_9^\alpha) + 2L_\sigma(G_4^\alpha - r_0 G_5^\alpha). \tag{3.45}$$

The leading singular exponent, namely, $1+(1/\delta)$, is evidently the same as in the symmetric case, while the amplitude, $\tilde{m}_2^\alpha$, is

$$\tilde{m}_2^\alpha = 2(jJ_1 - J)[-G_4^\alpha + r_0 G_5^\alpha - \tilde{m}_1^\alpha(-G_5^\alpha + L_\sigma G_4^\alpha)/\chi_e^\alpha]. \tag{3.46}$$

Recall that the coefficients j, J_1, and J are defined above in Sec. III C.

The leading correction exponent is now just that found by Klinger[9] in his classical treatment; it does *not* appear in the symmetric case. The expression for its amplitude, $\tilde{m}_3^\alpha$, is complicated but, for the record, we quote the result, namely,

$$\tilde{m}_3^\alpha = \frac{(\delta+1)}{\delta}\left(\frac{\chi_1^\alpha}{\chi_e^\alpha}\right)\left[\tilde{m}_1^\alpha \frac{\chi_1^\alpha}{\chi_e^\alpha} - 2(jJ_1 - J)(-G_4^\alpha + r_0 G_5^\alpha)\right] + 2\,\mathrm{sgn}(j_1) g_2\left[(-G_5^\alpha + L_\sigma G_4^\alpha)\frac{\tilde{m}_1^\alpha}{\chi_e^\alpha} - (-G_4^\alpha + r_0 G_5^\alpha)\right], \tag{3.47}$$

where the new coefficients are

$$\chi_1^\alpha = 2(-G_5^\alpha + L_\sigma G_4^\alpha)(jJ_1 - J), \tag{3.48}$$

$$g_2 = r_0^2 |j_1|^{3+(2/\delta)} J^2 J_1 - \frac{(\delta+1)}{\delta}|j_1|^{1/\delta} jJ. \tag{3.49}$$

E. Critical endpoint binodals

Now we conclude our discussion of the endpoint itself by presenting, finally, the shape of the critical phase binodals, $\mathcal{B}_e^\beta$ and $\mathcal{B}_e^\gamma$. These can be obtained by using the thermodynamic potential for the critical phase, $G^{\beta\gamma}(g,t,h)$, and the endpoint phase boundary, $g_\sigma(\tilde{h})$. Details are given in Sec. IV D. As discussed before, it is convenient to describe the binodals with the aid of a parameter s (in this case, related to $|\tilde{h}|^{\beta/\Delta}$) which vanishes at the endpoint and increases in the β and γ phases.

In the *symmetric* case, **S**, the critical endpoint binodals may then be specified by

$$\begin{aligned} m = {} & \pm Es[1 + u_4 s^{\theta_4/\beta} + u_1 s^{(1-\alpha)/\beta} + \cdots] \\ & \pm V_1 s^{\Delta/\beta}[1 + v_1 s^{\Delta/\beta} + \cdots] \pm V_2 s^{(1-\alpha+\Delta)/\beta}[1+\cdots] \\ & \pm V_3 s^{(2-\alpha+\Delta)/\beta}[1+\cdots], \end{aligned} \tag{3.50}$$

$$\begin{aligned} \tilde{m} = {} & \tilde{E} s^{(1-\alpha)/\beta}[1 + \tilde{u}_4 s^{\theta_4/\beta} + \tilde{u}_1 s^{(1-\alpha)/\beta} + \cdots] \\ & + \tilde{V} s^{(2-\alpha)/\beta}[1+\cdots], \end{aligned} \tag{3.51}$$

where $\pm$ corresponds to $\tilde{h} \gtrless 0$, and the coefficients are given in (4.58) and (4.59).

The *symmetric* critical endpoint binodals may finally be expressed in terms of m as a variable by solving (3.50) for s and substituting in (3.51). With $x = |m/E|$ this yields

$$\tilde{m} = \tilde{E} x^{(1-\alpha)/\beta}[1 + \overline{u_4} x^{\theta_4/\beta} + \overline{u_1} x^{(1-\alpha)/\beta} + \cdots], \tag{3.52}$$

where

$$\overline{u_1} = \tilde{u}_1 - (1-\alpha)u_1/\beta, \quad \overline{u_4} = \tilde{u}_4 - (1-\alpha)u_4/\beta. \tag{3.53}$$

The term in $\tilde{E}$ provides the dominant behavior with the same exponent as the λ-line binodals given in Sec. III B. One should note that the amplitude $\tilde{E}$ is negative in case **A** while it is positive in case **B** due to the negative sign of w_1^0 discussed following (2.23).[17] Hence it has the same sign as the amplitude $\tilde{A}$ of the lambda-line binodals; see (3.10). This also holds in the nonsymmetric case.

Indeed, the *nonsymmetric*, **N**, critical endpoint binodals may be described similarly. In terms of the parameter s we find

$$\begin{aligned} m = {} & \pm Es[1 \pm u_1 s^{(\Delta-1)/\beta} + u_2 s^{(1-\alpha)/\beta} + \cdots + u_4 s^{\theta_4/\beta} + \cdots \\ & \pm u_5 s^{\theta_5/\beta} + \cdots] + V_1 s^{(1-\alpha)/\beta}[1 \pm v_1 s^{(\Delta-1)/\beta} \\ & + v_2 s^{(1-\alpha)/\beta} + \cdots + v_4 s^{\theta_4/\beta} + \cdots \pm v_5 s^{\theta_5/\beta} + \cdots] \\ & \pm V_2 s^{\Delta/\beta}[1 \pm v_0 s \cdots] + V_3 s^{(2-\alpha)/\beta}[1+\cdots], \end{aligned} \tag{3.54}$$

$$\begin{aligned} \tilde{m} = {} & \tilde{E} s^{(1-\alpha)/\beta}[1 \pm \tilde{u}_1 s^{(\Delta-1)/\beta} + \tilde{u}_2 s^{(1-\alpha)/\beta} + \cdots \\ & + \tilde{u}_4 s^{\theta_4/\beta} + \cdots \pm \tilde{u}_5 s^{\theta_5/\beta} + \cdots] \\ & \pm \tilde{V}_1 s^{\Delta/\beta}[1 \pm \tilde{v}_0 s + \cdots] \\ & + \tilde{V}_2 s^{(2-\alpha)/\beta}[1+\cdots], \end{aligned} \tag{3.55}$$

where the leading coefficients are presented in (4.60)–(4.62). Solving for s in (3.54) and substituting into (3.55), one finally obtains

$$\tilde{m} = \tilde{E} x^{(1-\alpha)/\beta}[1 + \overline{u_4} x^{\theta_4/\beta} \pm \overline{u_1} x^{(\Delta-1)/\beta} \pm \overline{u_2} x^{(1-\alpha)/\beta} + \cdots], \tag{3.56}$$

where the leading coefficients are

$$\begin{aligned} & \overline{u_1} = \tilde{u}_1 - (1-\alpha)(E/V_1 + u_1)/\beta, \\ & \overline{u_2} = \tilde{V}_1/\tilde{E}, \quad \overline{u_4} = \tilde{u}_4 - (1-\alpha)u_4/\beta, \end{aligned} \tag{3.57}$$

while the correction factor exponents have $d=3$ Ising values $\theta_4/\beta \simeq 1.66$, $(\Delta-1)/\beta \simeq 1.73$, and $(1-\alpha)/\beta \simeq 2.73$.

F. Binodals above the endpoint temperature

Let us consider first the *spectator-phase binodal* $\mathcal{B}^\alpha$ above T_e [see Figs. 3(c) and 6(c)] which is the simplest to analyze. Since $G^\alpha(g,t,h)$ is noncritical, the densities m and $\tilde{m}$ are *noncritical* functions of g, t, and h in the spectator-phase α. At fixed $t>0$, the phase boundary $g_\sigma(t;h)$ is also a nonsingular function of h with t-dependent expansion coefficients, which are discussed explicitly below in Sec. IV E. Consequently, on the isotherms above T_e, the α binodal becomes noncritical. However, singularities of the binodal are to be expected as $T \to T_e+$.

In the *symmetric case*, by using the previous definitions (3.34) and (3.35) and the phase boundary $g_\sigma(t;h)$ given below in (4.67), we obtain

$$\tilde{m}=\tilde{m}_e^\alpha-\tilde{\chi}_e^\alpha(g_{\sigma,0}^+t+g_{\sigma,1}^+t^{2-\alpha})-\tilde{\chi}_e^\alpha g_{\sigma,3}^+t^{-\gamma}x_\alpha^2+\cdots, \tag{3.58}$$

where $x_\alpha=m/\chi_e^\alpha$, as for the symmetric noncritical endpoint binodals in (3.36), while the coefficients, $g_{\sigma,0}^+$, etc. are given below in (4.68). Note that the curvature of the binodal diverges as $t^{-\gamma}$ when $T\to T_e+$.

In the *nonsymmetric case*, using (4.70), we obtain

$$\tilde{m}=\tilde{m}_e^\alpha+\tilde{m}_1^\alpha x_\alpha+\tilde{m}_2^\alpha(t)x_\alpha^2+\cdots, \tag{3.59}$$

where $\tilde{m}_e$ and $\tilde{m}_1^\alpha$ are given above in (3.43) and (3.45), respectively, while the coefficient of second order in x_α $(=m/\chi_e^\alpha)$ is

$$\tilde{m}_2^\alpha(t)=2(G_4^\alpha-L_\rho G_5^\alpha)g_{\sigma,3}^+\,j_1^2t^{-\gamma}+\cdots, \tag{3.60}$$

where $g_{\sigma,3}^+$ is given below in (4.71). Here we have neglected higher order corrections in t. Just as in the symmetric case, the curvature of the binodal diverges when $T\to T_e+$.

Consider next the *critical phase binodal* $\mathcal{B}^{\beta\gamma}$ above T_e; see Figs. 3(c) and 6(c). This may be determined using (4.15) below and its twin for $\tilde{m}$ with the aid of the spectator-phase boundary, $g_\sigma(t;\tilde{h})$, which is derived in Sec. IV E. For fixed $t>0$, the small y expansion for the scaling function $W_+(y,y_4,\ldots)$ yields only integer powers of $\tilde{h}$ in (4.15) and its twin so that the densities m and $\tilde{m}$ are noncritical functions of $\tilde{h}$. Consequently, the critical phase binodal is again noncritical above T_e.

In the *symmetric case*, the densities m and $\tilde{m}$ can be written in terms of $\tilde{h}$ by using (4.15) and its twin as

$$m=l_1t^{-\gamma}\tilde{h}+\cdots, \tag{3.61}$$

$$\tilde{m}=\tilde{m}_0(t)+\tilde{l}_2t^{-\gamma-1}\tilde{h}^2+\cdots, \tag{3.62}$$

where $\tilde{m}_0(t)$ is a function of t only while the coefficients are

$$\begin{aligned} l_1&=2Q_eU^2W_{+2}^0|1-q_1(D_2/D_1)|^{-\gamma},\\ \tilde{l}_2&=-\gamma q_1Q_eU^2W_{+2}^0|1-q_1(D_1/D_2)|^{-\gamma-1}. \end{aligned} \tag{3.63}$$

Notice that $\tilde{l}_2$ is negative in case **A** while it is positive in case **B**, as for $\tilde{A}$, the leading amplitude of the lambda line binodals; see the paragraph below (3.9). We may eliminate $\tilde{h}$ between (3.61) and (3.62) and write the binodal in terms of $x=m/l_1$, noticing $l_1>0$, as

$$\tilde{m}=\tilde{m}_0(t)+\tilde{l}_2t^{\gamma-1}x^2+\cdots. \tag{3.64}$$

Since $\gamma>1$ in the $d<4$ Ising universality classes, the coefficient of the quadratic term in x vanishes as $T\to T_e+$. This result could be anticipated, since the critical endpoint binodals have the leading exponent $(1-\alpha)/\beta$ ($\simeq 2.73$) in the symmetric case. Thus the curvature of $\mathcal{B}^{\beta\gamma}$ is singular but *non*divergent when $T\to T_e$.

In the general *nonsymmetric case*, the situation is more complicated. The densities can now be expressed as

$$m=m_0(t)+l_1t^{-\gamma}\tilde{h}+l_2t^{-\gamma-1}\tilde{h}^2+\cdots, \tag{3.65}$$

$$\tilde{m}=\tilde{m}_0(t)+\tilde{l}_1t^{1-\alpha}\tilde{h}+\tilde{l}_2t^{-\gamma-1}\tilde{h}^2+\cdots, \tag{3.66}$$

where the constant coefficients are presented below in (4.74). Note that the term linear in $\tilde{h}$ for $\tilde{m}$ has a leading t-dependent coefficient that vanishes when $T\to T_e+$. As before, the critical phase binodal can be written in terms of $x=\Delta m/l_1$ with $\Delta m\equiv m-m_0(t)$ as

$$\tilde{m}=\tilde{m}_0(t)+\tilde{l}_1t^{1+2\gamma-\alpha}x+\tilde{l}_2t^{\gamma-1}x^2+\cdots. \tag{3.67}$$

Evidently, both the coefficients of x and x^2 are singular but vanish when $T\to T_e+$ and $\gamma>1$.

G. Binodals below the endpoint temperature

Below the endpoint temperature three phases, α, β, and γ, may coexist on the triple line τ. The binodals near a triple point then spring from the corners of a three-phase triangle. The corresponding phase diagrams in the density plane are shown in Figs. 3(a) and 6(a) for the two cases **NA** and **SB**, respectively. Thermodynamic stability then requires that these diagrams must satisfy Schreinemakers' rules;[5,17–19] details are given in Ref. 17.

The explicit forms of the *spectator-phase binodals*, $\mathcal{B}_<^{\alpha\pm}$, can be obtained without difficulty by using the phase boundary $g_\sigma(t,h)$ below T_e as presented in (4.76) and (4.79) for the symmetric and nonsymmetric cases, respectively. In the *symmetric case*, the binodal may be expressed as

$$\tilde{m}=\tilde{m}_e^\alpha-\tilde{\chi}_e^\alpha g_{\sigma,0}^-t\mp\tilde{\chi}_e^\alpha g_{\sigma,2}^-|t|^\beta x_\alpha-\tilde{\chi}_e^\alpha g_{\sigma,3}^-|t|^{-\gamma}x_\alpha^2+\cdots, \tag{3.68}$$

where $x_\alpha=m/\chi_e^\alpha$ and the upper (lower) sign corresponds to $m>0$ (<0), while the coefficients, $g_{\sigma,0}^-$, etc., are given below in (4.77). Note that the slope vanishes as $T\to T_e-$ while the curvature diverges as $|t|^{-\gamma}$. In the *nonsymmetric case*, the binodal is given by

$$\tilde{m}=\tilde{m}_e^\alpha+\tilde{m}_1^\alpha(t)x_\alpha+\tilde{m}_2^\alpha(t)x_\alpha^2+\cdots, \tag{3.69}$$

where the coefficients are

$$\begin{aligned} \tilde{m}_1^\alpha(t)&=\tilde{m}_1^\alpha\mp 2g_{\sigma,2}^-j_1(-G_4^\alpha+L_\rho G_5^\alpha)|t|^\beta+\cdots,\\ \tilde{m}_2^\alpha(t)&=-2g_{\sigma,3}^-j_1^2(-G_4^\alpha+L_\rho G_5^\alpha)|t|^{-\gamma}+\cdots, \end{aligned} \tag{3.70}$$

while the $\mp$ signs again correspond to $m\gtrless 0$. The coefficients, $g_{\sigma,0}^-$, etc., are given below in (4.80). Notice that the linear terms do not vanish, but approach the same value when $T\to T_e-$.

The *critical phase binodals*, $\mathcal{B}_<^\beta$ and $\mathcal{B}_<^\gamma$, can be obtained, in principle, by using (4.15) and its twin with the aid of the phase boundary $g_\sigma(t,h)$ given below in (4.76) and (4.79). However, the analysis becomes more complicated, since these binodals are associated with the lambda-line binodals near the vertices of the three-phase triangle; see Figs. 3(a) and 6(a). Hence, we do not present their explicit forms here. One can anticipate, however, that the binodals have linear slopes and quadratic terms which both vanish when $T\to T_e-$ in the $d<4$ Ising universality classes.

IV. DERIVATION OF THE BINODAL EXPRESSIONS

Here we sketch, for completeness, some of the details that enter into the derivation of the results for the binodals presented in Sec. III from the postulates of Sec. II. In addition, we give explicit expressions for the leading amplitudes entering the formulas of Sec. III in terms of the original parameters of the postulated free energies of Sec. II.

A. Principles for obtaining isothermal sections

Our aim is to describe isothermal sections of the full (g,t,h) phase space in terms of the density variables,

$$\rho_1=-\partial_h G, \quad \rho_2=-\partial_g G \quad \text{with} \quad \partial_h\equiv\partial/\partial h, \quad \partial_g\equiv\partial/\partial g. \tag{4.1}$$

Accordingly, we treat t as a fixed parameter and regard only g and h as varying. The basic nonlinear scaling fields $\tilde{t}$ and $\tilde{h}$ are then to be viewed as functions only of g and h. Once the appropriate derivatives with respect to g and h have been performed, however, it is more convenient, in light of the scaling postulate (2.13), to employ the nonlinear scaling fields $\tilde{t}$ and $\tilde{h}$ as the primary field variables. Note, in particular, that both the λ line and the triple line, τ, lie in the plane $\tilde{h}=0$. Beyond that, the λ-line or ρ-surface binodals also correspond to $\tilde{h}=0$ while the spectator-phase and σ binodals are of interest only for small $\tilde{h}$. Consequently we express g and h in terms of $\tilde{t}$ and $\tilde{h}$ via the noncritical expansions,

$$g=g_\lambda(t)+e_1\tilde{t}+e_2\tilde{h}+e_3\tilde{t}^{\,2}+e_4\tilde{t}\tilde{h}+e_5\tilde{h}^2+\cdots, \tag{4.2}$$

$$h=h_\lambda(t)+f_1\tilde{t}+f_2\tilde{h}+f_3\tilde{t}^{\,2}+f_4\tilde{t}\tilde{h}+f_5\tilde{h}^2+\cdots, \tag{4.3}$$

where the λ-line values, g_λ and h_λ, were introduced in (2.8) and are seen to be noncritical functions. Likewise, all the coefficients, $e_j(t)$ and $f_j(t)$, are noncritical with, in the symmetric case,

$$\mathbf{S}:\ e_2=e_4=f_1=f_3=f_5=0,$$
$$e_1=q_1^{-1}+O(t), \quad f_2=1, \quad e_3=-\frac{q_2}{q_1^3},$$
$$e_5=-\frac{q_6}{q_1}, \quad f_4=-\frac{r_1}{q_1}. \tag{4.4}$$

More generally, with $\Lambda_0\equiv q_1-r_0q_0\,(\neq 0)$, we have

$$\mathbf{N}:\ e_1,e_2,f_1,f_2=(1,-q_0,-r_0,q_1)/\Lambda_0+O(t), \tag{4.5}$$

while $e_3,\ldots,f_5$ are also readily found in terms of the q_j and r_j.

Any noncritical property $P(g,t,h)$ with expansion (2.2) can then be rewritten as

$$P(g,t,h)=P_\lambda(t)+\dot{P}_1(t)\tilde{t}+\dot{P}_2(t)\tilde{h}+\dot{P}_3(t)\tilde{t}^{\,2}+\cdots, \tag{4.6}$$

where the value on the λ line is given by

$$P_\lambda(t)=P_e+P_{\lambda 1}t+P_{\lambda 2}t^2+\cdots, \tag{4.7}$$

$$P_{\lambda 1}=P_1\Lambda_g+P_2+P_3\Lambda_h,$$
$$P_{\lambda 2}=P_1\Lambda_{g2}+\cdots+P_9\Lambda_h^2,\cdots, \tag{4.8}$$

where Λ_g, Λ_h, Λ_{g2}, etc. are defined in (2.8) and (2.9), while the remaining noncritical coefficients take the form

$$\dot{P}_j(t)=\dot{P}_{je}+\dot{P}_{j1}t+\dot{P}_{j2}t^2+\cdots,$$
$$\dot{P}_{je}=P_1e_j+P_3f_j, \tag{4.9}$$

$$\dot{P}_{j1}=2(P_4\Lambda_g e_j+P_5\Lambda_g f_j+P_5\Lambda_h e_j+P_6e_j+P_7f_j+P_9\Lambda_h f_j), \tag{4.10}$$

for $j=1$ or 2, and

$$\dot{P}_{3e}=P_1e_3+P_3f_3+P_4e_1^2+2P_5e_1f_1+P_9f_1^2, \tag{4.11}$$

and so on.

Of course, we eventually wish to eliminate $\tilde{t}$ and $\tilde{h}$ in favor of ρ_1 and ρ_2 or, in view of the discussion in Sec. III A, in terms of

$$m=-\partial G+(\partial G)_e, \quad \tilde{m}=-\tilde{\partial}G+(\tilde{\partial}G)_e, \tag{4.12}$$

where the compound differential operators are

$$\partial=\partial_h-L_\sigma\partial_g, \quad \tilde{\partial}=\partial_g-L_\rho\partial_h. \tag{4.13}$$

However, once we have expressions for m and $\tilde{m}$ in terms of $\tilde{t}$ and $\tilde{h}$ we can regard these fields merely as auxiliary *parameters* relating m and $\tilde{m}$. Note in particular that coexisting phases must have the same values of $\tilde{t}$ and $\tilde{h}$. Thus for the ρ binodals we can put $s=(-\tilde{t})^\beta$, for $\tilde{t}<0$, and set $\tilde{h}=0$. This indicates the origin of the parametric descriptions of the binodals presented in Sec. III B. Similarly, for the binodals associated with the σ phase boundary, equating the free energies $G^{\beta\gamma}$ and G^α gives a relation for $\tilde{t}$ in terms of $\tilde{h}$ (and t): then $\tilde{h}$ is an appropriate parameter.

The axis slopes L_σ and L_ρ in (4.13) were explained in Sec. III A and the slope L_σ was given in (3.42). Below we will establish the t-dependent result,

$$L_\rho(t)=r_0+[2r_4\Lambda_g+r_5+r_1\Lambda_h-r_0(r_1\Lambda_g+r_2+2r_3\Lambda_h)]t+O(t^2), \tag{4.14}$$

where $L_\rho(t)$ was introduced just before (3.13) and $L_\rho\equiv L_\rho(0)=r_0$.

Now using (4.12) and (2.13) we obtain the primary density in the form

$$m=(\partial G^0)_e-\partial G^0+|\tilde{t}|^{2-\alpha}\Big[(\partial Q)W_\pm+\sum_{k\geqslant 4}(\partial U_k)QW_\pm'^{(k)}|\tilde{t}|^{\theta_k}\Big]\pm(\partial\tilde{t})|\tilde{t}|^{1-\alpha}Q\dot{W}_\pm\mp(\partial\tilde{t})\tilde{h}|\tilde{t}|^{\beta-1}\Delta QUW_\pm'+(\partial\tilde{h})|\tilde{t}|^\beta QUW_\pm', \tag{4.15}$$

for $\tilde{h}\to 0$, with a precisely similar expression for $\tilde{m}$ with $\tilde{\partial}$ replacing ∂, while

$$\dot{W}_\pm(y,y_4,\ldots)=(2-\alpha)W_\pm+\sum_{k\geqslant 4}\theta_kU_kW_\pm'^{(k)}|\tilde{t}|^{\theta_k}, \tag{4.16}$$

$$W'_{\pm}(y,y_4,\ldots)=(\partial W_{\pm}/\partial y), \quad W'^{(k)}_{\pm}(y,\ldots)=(\partial W_{\pm}/\partial y_k). \tag{4.17}$$

Note that ∂G^0 and the coefficients ∂Q, ∂U_k, $\partial\tilde{t}$, and $\partial\tilde{h}$ are all noncritical and so can be written as in (4.6). This form thus enables one to identify all the singular terms appearing in m and $\tilde{m}$.

Now on the λ line we have $\tilde{t}=\tilde{h}=0$. Thus (4.15) and its twin for $\tilde{m}$ yield the expansions (3.4) and (3.5) for m_λ and $\tilde{m}_\lambda$ with

$$M_1=2[L_\sigma(\Lambda_g G_4^0+\Lambda_h G_5^0+G_6^0)-\Lambda_g G_5^0-G_7^0-\Lambda_h G_9^0], \tag{4.18}$$

$$\tilde{M}_1=2[L_\rho(\Lambda_g G_5^0+G_7^0+\Lambda_h G_9^0)-\Lambda_g G_4^0-\Lambda_h G_5^0-G_6^0], \tag{4.19}$$

so that $M_1=0$ and $\tilde{M}_1=2(G_4^0/q_1-G_6^0)$ in the symmetric case. Defining $R(g,t,h)=(\partial G^0)_e-\partial G^0$ and $\tilde{R}$ likewise, and expanding as in (4.6) yields, for $j=1$, 2,

$$\dot{R}_j=2[L_\sigma(G_4^0 e_j+G_5^0 f_j)-G_5^0 e_j-G_9^0 f_j]+O(t), \tag{4.20}$$

$$\dot{\tilde{R}}_j=2[r_0(G_5^0 e_j+G_9^0 f_j)-G_4^0 e_j-G_5^0 f_j]+O(t), \tag{4.21}$$

where (4.14) was used for L_ρ. For reference below we also record

$$(\partial\tilde{t})_\lambda=q_0-L_\sigma q_1+[q_5\Lambda_g+2q_6\Lambda_h+q_7 -L_\sigma(2q_2\Lambda_g+q_3+q_5\Lambda_h)]t+\cdots, \tag{4.22}$$

$$(\partial\tilde{h})_\lambda=1-L_\sigma r_0+[r_1\Lambda_g+r_2+2r_3\Lambda_h -L_\sigma(r_1\Lambda_h+2r_4\Lambda_g+r_5)]t+\cdots, \tag{4.23}$$

$$(\tilde{\partial}\tilde{t})_\lambda=q_1-r_0 q_0+[2q_2\Lambda_g+q_3+q_5\Lambda_h -L_\rho(q_5\Lambda_g+2q_6\Lambda_7+q_7)]t+\cdots, \tag{4.24}$$

$$(\tilde{\partial}\tilde{h})_\lambda=r_0-L_\rho+[r_1\Lambda_h+2r_4\Lambda_g+r_5 -L_\rho(r_1\Lambda_g+r_2+2r_3\Lambda_h)]t+\cdots. \tag{4.25}$$

Clearly, any desired higher order terms in the $\tilde{t}$, $\tilde{h}$ expansions can be obtained straightforwardly. Finally, we remark that we will shortly see that the condition determining $L_\rho(t)$ is that $(\tilde{\partial}\tilde{h})_\lambda$ vanishes term by term; substitution of (4.14) in (4.25) checks this.

B. Derivation of the λ-line binodals

The binodals associated with the λ line may, essentially, be obtained directly from (4.15) and its twin by letting $\tilde{h}\to 0\pm$ with $\tilde{t}<0$. In doing this the small y expansions (2.21) must be used with attention to the $\sigma_{\boldsymbol{\kappa}}(y)$ factors defined in (2.22). When this is done the G^0 terms in (4.15) generate only integral powers of $|\tilde{t}|$; the terms in $|\tilde{t}|^{2-\alpha}$ act merely to modify the correction factor of the $|\tilde{t}|^{1-\alpha}$ term. Note that the $\tilde{t}$ and $\tilde{h}$ expansions of Q and of the U_k yield correction terms varying as $|\tilde{t}|^{n+\theta[\boldsymbol{\kappa}]}$ for all integers $n\geqslant 0$ and all $\boldsymbol{\kappa}>0$. The term in $\tilde{h}|\tilde{t}|^{\beta-1}$, which diverges as $|\tilde{t}|\to 0$, vanishes identically. Lastly, the term in $|\tilde{t}|^{\beta}$ contributes both to m and $\tilde{m}$.

Introducing the parameter $s=|\tilde{t}|^{\beta}$ then yields the previously quoted expansions (3.6) and (3.7) for m and $\tilde{m}$ in the symmetric case. The linear term in s is absent in this $\tilde{m}$ expansion because the coefficient $(\partial_g\tilde{h})$ vanishes identically by symmetry when $h\equiv\tilde{h}\to 0$ and $L_\rho=0$ is dictated. Similarly, terms varying as $s^{1/\beta}$ and $s^{(1-\alpha)/\beta}$ are absent in the expression for m since $L_\sigma=0$ and thence ∂G^0, ∂Q, and $\partial\tilde{t}$ all vanish. For *even* k the derivatives $\partial_h U_k=\partial U_k$ (for $L_\sigma=h=0$) also vanish by symmetry. However, in the fully symmetric situation each odd scaling field, $U_{2j+1}(g,t,h)$, must itself be odd in h: see (2.12). Hence after operating with ∂_h, contributions with *odd* k in the terms proportional to $|\tilde{t}|^{2-\alpha+\theta_k}(\partial U_k)$ in (4.15) appear in the expansion for m in the symmetric case. Since $2-\alpha=\beta+\Delta$ these terms are responsible for the appearance of the correction factors $|\tilde{t}|^{\Delta}=s^{\delta}$ in (3.6); see also (3.9). For completeness we record the leading amplitude values,

$$\tilde{A}_e=-(2-\alpha)q_1 Q_e W_{-0}^0, \quad B_e=UQ_e W_{-1}^0, \quad \tilde{K}_e=2G_4^0/q_1, \tag{4.26}$$

$$\tilde{a}_{4e}=\left(1+\frac{\theta_4}{2-\alpha}\right)\frac{W_{-0}^{(4)}}{W_{-0}^0}U_{4e}, \quad b_{4e}=\frac{W_{-1}^{(4)}}{W_{-1}^0}U_{4e}. \tag{4.27}$$

Clearly all other amplitudes are readily generated although their complexity increases rapidly with order.

In the general *nonsymmetric case* the U_k for odd k need not vanish when $\tilde{h}\to 0$ but the scaling function, $W_-(y,y_4,y_5,\ldots)$, still has special behavior for small y_k when k is odd: see (2.18). This is the reason why the $\pm$ signs (corresponding to $\tilde{h}\to 0\pm$) appear in the expansion (3.11) for m. The expansion for the secondary density $\tilde{m}$, when initially generated, has a similar structure. In particular, the leading term is proportional to $|\tilde{t}|^{\beta}\equiv s$. However, at this point we should, as explained in Sec. III A, complete the specification of the density $\tilde{m}$ by appropriately choosing $L_\rho(t)$. This should be done by examining the common tangent to the critical binodals, namely, $\mathcal{B}_e^{\beta}$ and $\mathcal{B}_e^{\gamma}$, at the endpoint; see Figs. 3(b) and 6(b). But these binodals involve the σ phase boundary which we have not yet studied. Instead, we will select L_ρ so that the common tangent of the λ-line binodals $\mathcal{B}_e^{\lambda+}$ and $\mathcal{B}_e^{\lambda-}$ or $\mathcal{B}_>^{\lambda+}$ and $\mathcal{B}_>^{\lambda-}$ coincides with the $\tilde{m}=0$ axis when extrapolated to the endpoint. It will be confirmed below that this criterion gives the same value for L_ρ. The coefficient of the offending $|\tilde{t}|^{\beta}$ term is $(\tilde{\partial}\tilde{h})_e$: see (4.25). This vanishes when $L_\rho=r_0$ thereby confirming (4.14) for $t=0$.

The residual t and $|\tilde{t}|$ dependence of $(\tilde{\partial}\tilde{h})$ then yield the $B'ts$ and $\tilde{B}s^{(1+\beta)/\beta}$ terms in the expansion (3.12) for $\tilde{m}$. The latter term is unavoidable in general and further complicates the singular corrections to the ρ binodals in the nonsymmetric case. Nevertheless, as explained in Sec. III B, the former term, linear in s, can be eliminated by adopting a temperature-dependent definition for $\tilde{m}$ by allowing L_ρ to vary noncritically with T. The criterion now is to make $(\tilde{\partial}\tilde{h})_\lambda(t)$ vanish. Reference to (4.25) then confirms the leading term in $L_\rho(t)$ presented in (4.14).

The leading amplitudes in (3.11) and (3.12) for the nonsymmetric case are, recalling (4.20)–(4.25) and (4.27),

$$A(t),\quad \tilde{A}(t) = -(2-\alpha)Q_\lambda W^0_{-0}[(\partial\tilde{t})_\lambda,(\tilde{\partial}\tilde{t})_\lambda], \tag{4.28}$$

$$B(t) = Q_\lambda U W^0_{-1}(\partial\tilde{h})_\lambda, \tag{4.29}$$

$$\tilde{B}_e = -Q_e U W^0_{-1}[(2r_4 - r_0 r_1)e_1 + (r_1 - 2r_0 r_3)f_1], \tag{4.30}$$

$$K_e = -\dot{R}_{1e},\quad \tilde{K}_e = -\dot{\tilde{R}}_{1e},\quad \tilde{a}_4 = a_4,\quad \tilde{b}_4 = b_4. \tag{4.31}$$

One further has $\tilde{a}_5 = a_5$, $\tilde{b}_5 = b_5$, etc., although correction terms carrying "noncritical factors" $s^{1/\beta} \equiv |\tilde{t}|$ do *not*, in general, satisfy corresponding equalities.

C. Spectator phase boundary: Endpoint isotherm

As indicated in Sec. III C, the first step in studying the binodals not associated with the λ line is to obtain the phase boundary σ as specified by $g_\sigma(t,h)$. On recalling (2.26) and (2.13), one sees this is to be found by solving

$$D(g,t,h) = -Q|\tilde{t}|^{2-\alpha} W_\pm(y,y_4,\ldots), \tag{4.32}$$

where $D(g,t,h)$ is noncritical with $D_e = 0$ and $D_1 > 0$. Here we focus only on the endpoint isotherm, $T = T_e$ or $t = 0$. Now consider the argument y in leading order, using (2.5) and (2.6):

$$y = U\tilde{h}/|\tilde{t}|^\Delta \approx U(h + r_0 g)/|q_0 h + q_1 g|^\Delta. \tag{4.33}$$

If r_0, q_0, and q_1 do not vanish (as in the generic *non*symmetric case), it is evident that when g, $h \to 0$ on σ one, in general, has $y \sim [\max(|g|,|h|)]^{1-\Delta}$ which diverges to ∞ since $\Delta > 1$. Thus to study (4.32) on the endpoint isotherm we must utilize the large y expansions (2.23) for the scaling functions entering (2.15). In the symmetric case one actually has $r_0 = q_0 = 0$; but it then transpires, as shown below, that $g_\sigma \sim |h|^{(2-\alpha)/\Delta}$ so that $y \sim |h|^{\alpha-1}$. Since $\alpha < 1$ we see that y again diverges. Thus in (4.32) we must always use the expansion

$$\begin{aligned} W_\pm = {} & W^0_\infty |y|^{(2-\alpha)/\Delta}(1 \pm w^0_1|y|^{-1/\Delta} + w^0_2|y|^{-2/\Delta} \pm \cdots) \\ & + W^{(4)}_\infty y_4 |y|^{(2-\alpha+\theta_4)/\Delta}(1 \pm w^{(4)}_1|y|^{-1/\Delta} + \cdots) \\ & + W^{(5)}_\infty y_5\,\mathrm{sgn}(y)|y|^{(2-\alpha+\theta_5)/\Delta}(1 \pm w^{(5)}_1|y|^{-1/\Delta} + \cdots) \\ & + \cdots, \end{aligned} \tag{4.34}$$

where the $\pm$ signs correspond to $\tilde{t} \gtrless 0$.

The analysis is considerably simpler if one uses $\tilde{h}$ as a variable in place of h. To this end we rearrange (2.5) and (2.6) with $t = 0$ to obtain

$$h = \tilde{h} - r_0 g - (r_1 - 2r_0 r_3)g\tilde{h} - r_3\tilde{h}^2 - \overline{r_4}g^2 + \cdots, \tag{4.35}$$

where $\overline{r_4} = r_4 - r_0 r_1 + r_3 r_0^2$, and

$$\tilde{t} = q_0\tilde{h} + p_1 g + p_2\tilde{h}^2 + p_3 g\tilde{h} + p_4 g^2 + \cdots, \tag{4.36}$$

where the leading coefficients are

$$\begin{aligned} & p_1 = q_1 - q_0 r_0, \quad p_2 = q_6 - q_0 r_3, \\ & p_3 = q_5 - q_0 r_1 + 2q_0 r_0 r_3 - 2q_6 r_0, \\ & p_4 = q_2 - q_5 r_0 + q_6 r_0^2 - q_0\overline{r_4}. \end{aligned} \tag{4.37}$$

Note that in the symmetric case one has $q_0 = q_5 = q_7 = 0$, $r_0 = r_3 = r_4 = 0$ and so $p_3 = 0$; we may suppose $p_1 \neq 0$.

Now, combining these results for the *symmetric case* yields the asymptotic equation,

$$D_1 g = -D_4 g^2 - D_9\tilde{h}^2 - (Q_e + Q_1 g + \cdots)|U\tilde{h}|^{(\delta+1)/\delta}Z - \cdots, \tag{4.38}$$

with the scaling factor, from (4.34),

$$\begin{aligned} Z = {} & W^0_\infty[1 \pm w^0_1|y|^{-1/\Delta} + w^0_2|y|^{-2/\Delta} \pm \cdots] \\ & + W^{(4)}_\infty U_4(g,0,h)|U\tilde{h}|^{\theta_4/\Delta}[1 \pm w^{(4)}_1|y|^{-1/\Delta} + \cdots] \\ & + \mathrm{sgn}(y)W^{(5)}_\infty U_5(g,0,h)|U\tilde{h}|^{\theta_5/\Delta}[1 \pm \cdots] + \cdots. \end{aligned} \tag{4.39}$$

These equations are to be solved together with

$$|y|^{-1/\Delta} = \frac{|\tilde{t}|}{|U\tilde{h}|^{1/\Delta}} = \frac{|q_1 g|}{|U\tilde{h}|^{1/\Delta}}\left[1 + \frac{q_2}{q_1}g + \frac{q_6}{q_1}\frac{\tilde{h}^2}{g} + \cdots\right], \tag{4.40}$$

to yield $g = g_\sigma(\tilde{h})$. This can be accomplished iteratively by noting that in leading order $g_\sigma \approx -J|\tilde{h}|^{(\delta+1)/\delta}$, where J was defined in (3.24); however, care is called for!

One obtains the result quoted in (3.22)–(3.25) which may be supplemented by

$$J_2 = D_9/D_1,\quad J_4 = [(D_4/D_1) - (Q_1/Q_e)]J^2, \tag{4.41}$$

$$c_3 = w^0_1(q_6 - q_1 J_2)/U^{1/\Delta},\quad c_4 = W^{(4)}_\infty U_{4e}U^{\theta_4/\Delta}/W^0_\infty, \tag{4.42}$$

$$c_4' = c_4 w^{(4)}_1|q_1|J/U^{1/\Delta},\quad c_5 = W^{(5)}_\infty U_{5,3}U^{\theta_5/\Delta}/W^0_\infty, \tag{4.43}$$

where $U_{5,3}$ is the first nonzero expansion coefficient of $U_5(g,0,h) \approx U_{5,3}h$ in the symmetric case. The expression (3.26) for $\tilde{h}(h)$ on σ follows from (2.6) and (3.22) by reversion.

The phase boundary in the *nonsymmetric case* follows in an analogous way but greater care is needed because of the increased number of nonvanishing and competing terms. Thus on the right side of (4.38) the new terms $-D_3\tilde{h}$ and $-2\overline{D_5}g\tilde{h}$ appear, where $\overline{D_5} = D_5 - \frac{1}{2}D_3(r_1 - 2r_0 r_3) - D_9 r_0$. The former term dominates and so in leading order one now finds

$$g_\sigma \approx -J_1\tilde{h} - J|\tilde{h}|^{(\delta+1)/\delta}, \tag{4.44}$$

where J_1 was defined in (3.27). This, in turn, yields the new behavior,

$$|y|^{-1/\Delta}=\frac{|\overline{q}|}{U^{1/\Delta}}|\tilde{h}|^{1-(1/\Delta)}\left[1-\tilde{\sigma}_h\frac{p_1}{\overline{q}}J|\tilde{h}|^{1/\delta}\mp\tilde{\sigma}_h\frac{p_1d_1}{\overline{q}}J|\tilde{h}|^{(1-\alpha)/\Delta}+\cdots\right],\tag{4.45}$$

where $\overline{q}=q_0-p_1J_1=\tilde{q}/j_1$ while $\tilde{q}$, j_1, and $\tilde{\sigma}_h$ were defined in (3.30) and (3.31).

In this way one obtains the result (3.28)–(3.32) which must be supplemented by new expressions for J_2 and J_3 while

$$d_2=w_2^0\overline{q}^2/U^{2/\Delta},\quad d_2'=2w_2^0p_1\overline{q}J/U^{2/\Delta},\quad d_2''=w_2^0p_1^2J^2/U^{2/\Delta}.\tag{4.46}$$

The expressions for d_3' and d_3'', are long and uninformative but we quote

$$d_3=w_3^0|\overline{q}|^3/U^{3/\Delta},\quad d_4=c_4,\quad d_4'=w_1^{(4)}d_4|\overline{q}|/U^{1/\Delta},$$
$$d_4''=w_1^{(4)}d_4p_1J/U^{1/\Delta},\quad d_5=W_\infty^{(5)}U_{5e}U^{\theta_5/\Delta}/W_\infty^0,\tag{4.47}$$
$$d_5'=w_1^{(5)}d_5|\overline{q}|/U^{1/\Delta},\quad d_5''=w_1^{(5)}d_5p_1J/U^{1/\Delta}.$$

Finally the remaining coefficients in (3.33) are

$$j'=r_0jJ|j_1|^{(\delta+1)/\delta},$$
$$j''=r_0j_1d_1J|j_1|^{(3-2\alpha-\beta)/\Delta},\tag{4.48}$$
$$j_2=j_1^3[r_0J_2+(r_1-2r_0r_3)J_1-r_3-\overline{r_4}J_1^2].$$

D. Derivation of the critical endpoint binodals

The critical phase binodals at the endpoint may be obtained from (4.15) and its twin using the endpoint isotherm, $g_\sigma(\tilde{h})$, obtained in the previous subsection. In order to do so, it is more convenient to rewrite (4.15) as

$$m=(\partial G^0)_e-(\partial G^0)+|\tilde{t}|^{2-\alpha}\left[(\partial Q)W_\pm+\sum_{k\geqslant 4}(\partial U_k)QW_\pm'^{(k)}|\tilde{t}|^{\theta_k}\right]\pm(\partial\tilde{t})Q|\tilde{t}|^{1-\alpha}\tilde{W}_\pm+(\partial\tilde{h})UQ|\tilde{t}|^{\beta}W_\pm',\tag{4.49}$$

and similarly for $\tilde{m}$ with $\tilde{\partial}$ replacing ∂, while

$$\tilde{W}_\pm=\dot{W}_\pm-\Delta yW_\pm',\tag{4.50}$$

where $\Delta=2-\alpha-\beta$ has been used. At the critical endpoint, $t=0$, we use $\tilde{h}$ as an auxiliary parameter relating m and $\tilde{m}$. Using (4.35) and (4.36), the noncritical functions, (∂G^0), (∂Q), etc., can be expressed in terms of $\tilde{h}$. Recalling the general expansion (2.2) for a noncritical function $P(g,t,h)$, we find, for $t=0$,

$$P(g,\ t=0,\ h)=P_e+P_3\tilde{h}+(P_1-r_0P_3)g_\sigma+\cdots,\tag{4.51}$$

and similarly for the derivatives,

$$\partial P=P_3-L_\sigma P_1+2(P_9-L_\sigma P_5)\tilde{h}+2(P_5-L_\sigma P_4-r_0P_9+r_0L_\sigma P_5)g_\sigma+\cdots,\tag{4.52}$$

$$\tilde{\partial}P=P_1-L_\rho P_3+2(P_5-L_\rho P_9)\tilde{h}+2(P_4-L_\rho P_5-r_0P_5+r_0L_\rho P_9)g_\sigma+\cdots.\tag{4.53}$$

Likewise, in terms of $g_\sigma(t=0,\ \tilde{h})$ we obtain

$$\partial\tilde{t}=q_0-L_\sigma q_1+(2q_6-L_\sigma q_5)\tilde{h}+(q_5-2L_\sigma q_2-2r_0q_6+L_\sigma r_0q_5)g_\sigma+\cdots,\tag{4.54}$$

$$\partial\tilde{h}=1-L_\sigma r_0+(2r_3-L_\sigma r_1)\tilde{h}+(r_1-2L_\sigma r_4-2r_0r_3+L_\sigma r_0r_1)g_\sigma+\cdots,\tag{4.55}$$

$$\tilde{\partial}\tilde{t}=q_1-L_\rho q_0+(q_5-2L_\rho q_6)\tilde{h}+(2q_2-L_\rho q_5-r_0q_5+2r_0L_\rho q_6)g_\sigma+\cdots,\tag{4.56}$$

$$\tilde{\partial}\tilde{h}=r_0-L_\rho+(r_1-2L_\rho r_3)\tilde{h}+(2r_4-L_\rho r_1-r_0r_1+2r_0L_\rho r_3)g_\sigma+\cdots.\tag{4.57}$$

As discussed before, the argument y of the scaling functions $W_\pm$ diverges to ∞ when the endpoint is approached on the σ surface. Thus in (4.49) and its twin the large y expansions (2.23) for the scaling functions must be used with attention to the $\sigma_{\boldsymbol{\kappa}}(y)$ factors defined in (2.22) and the multi-exponents $\theta[\boldsymbol{\kappa}]$ in (2.24). When this is done, we finally obtain the critical endpoint binodals from (4.49).

Introducing the parameter $s=|\tilde{h}|^{\beta/\Delta}$ then yields the previously quoted expansions (3.50) and (3.51) for m and $\tilde{m}$ in the *symmetric* case. The linear term in s is absent in the expression for $\tilde{m}$ when we choose $L_\rho(0)=r_0$ which reinforces previous results. In the expression for m the G^0 term in (4.49) provides a linear term in $\tilde{h}$ that yields the $s^{\Delta/\beta}$ term in (3.50); the terms in $|\tilde{t}|^{2-\alpha}$ provide the $s^{(2-\alpha+\Delta)/\beta}$ term and higher order corrections, since (∂Q) generates $\tilde{h}$ in leading order; the term in $|\tilde{t}|^{1-\alpha}$ provides the $s^{(1-\alpha+\Delta)/\beta}$ term for $(\partial\tilde{t})$ for the same reason; then, finally, the term in $|\tilde{t}|^{\beta}$ provides the leading s behavior. In the expression for $\tilde{m}$, all the terms, except for one in $|\tilde{t}|^{1-\alpha}$, provide correction terms, $s^{(2-\alpha)/\beta}$, in (3.51); the leading behavior, $s^{(1-\alpha)/\beta}$, is generated by the term in $|\tilde{t}|^{1-\alpha}$.

The leading amplitudes are

$$E=[(2-\alpha)/\Delta]Q_eW_\infty^0U^{(2-\alpha)/\Delta},\quad \tilde{E}=q_1Q_eW_\infty^0w_1^0U^{(1-\alpha)/\Delta}.\tag{4.58}$$

For the record, we also quote

$$V_1=-2G_9^0,\quad V_2=2q_6Q_eW_\infty^0w_1^0U^{(1-\alpha)/\Delta},$$
$$V_3=2Q_9W_\infty^0U^{(2-\alpha)/\Delta},$$
$$u_4=\frac{(2-\alpha+\theta_4)}{(2-\alpha)}\frac{W_\infty^{(4)}}{W_\infty^0}U_{4e}U^{\theta_4/\Delta},$$
$$u_1=-\frac{(1-\alpha)}{(2-\alpha)}w_1^0q_1J/U^{1/\Delta},\tag{4.59}$$
$$\tilde{u}_4=\frac{W_\infty^{(4)}w_1^{(4)}}{W_\infty^0w_1^0}U_{4e}U^{\theta_4/\Delta},\quad \tilde{u}_1=-2\frac{w_2^0q_1J}{w_1^0U^{1/\Delta}},$$
$$\tilde{V}=2G_4^0J+[Q_1+(2-\alpha)r_1Q_e/\Delta]W_\infty^0U^{(2-\alpha)/\Delta}.$$

In the general *nonsymmetric* case, the linear term in s is still absent in the expression for $\tilde{m}$: see (3.55). The expression for m in terms of s is given in (3.54); the G^0 terms in (4.49) yield the $s^{\Delta/\beta}$ term, as in the symmetric case, while the terms in $|\tilde{t}|^{2-\alpha}$ provide the $s^{(2-\alpha)/\beta}$ term and that in $|\tilde{t}|^{1-\alpha}$ gives $s^{(1-\alpha)/\beta}$; the leading term, s, is still provided by the term in $|\tilde{t}|^{\beta}$. In the expression for $\tilde{m}$ the leading behavior is $s^{(1-\alpha)/\beta}$, as in the symmetric case, again provided by the $|\tilde{t}|^{1-\alpha}$ term; the G^0 term yields corrections of leading order $s^{\Delta/\beta}$, while the terms in $|\tilde{t}|^{2-\alpha}$ and $|\tilde{t}|^{\beta}$ give the $s^{(2-\alpha)/\beta}$ term in (3.54). The required amplitudes are now

$$E=[(2-\alpha)/\Delta](1-L_\sigma r_0)Q_e W_\infty^0 U^{(2-\alpha)/\Delta},$$
$$\tilde{E}=(q_1-r_0q_0)Q_e W_\infty^0 w_1^0 U^{(1-\alpha)/\Delta}. \tag{4.60}$$

For the record, we also quote the correction amplitudes,

$$V_1=(q_0-L_\sigma q_1)Q_e W_\infty^0 w_1^0 U^{(1-\alpha)/\Delta},$$
$$V_2=-2(G_9^0-L_\sigma G_5^0)+2J_1(G_5^0-L_\sigma G_4^0-r_0G_9^0+r_0L_\sigma G_5^0),$$
$$V_3=(Q_3-L_\sigma Q_1)W_\infty^0 U^{(2-\alpha)/\Delta}, \tag{4.61}$$
$$\tilde{V}_1=-2(G_5^0-r_0G_9^0)+2J_1(G_4^0-2r_0G_5^0+r_0^2G_9^0),$$
$$\tilde{V}_2=[Q_1+(2-\alpha)(r_1-2r_0r_3)Q_e/\Delta]W_\infty^0 U^{(2-\alpha)/\Delta},$$

and the leading further coefficients

$$u_1=\frac{(1-\alpha)}{(2-\alpha)}\overline{q}w_1^0/U^{1/\Delta},\quad v_1=\tilde{u}_1=2\,\frac{w_2^0\overline{q}}{w_1^0U^{1/\Delta}}. \tag{4.62}$$

E. Spectator phase boundary: Isotherms above T_e

In Sec. IV C, we studied the endpoint isothermal phase boundary, $g_\sigma(h)$, in order to discuss the endpoint binodals. By the same token we study the phase boundary $g_\sigma(t,h)$ above T_e as the first step in determining the supercritical binodals. This boundary is found by equating the free energies, $G^\alpha(g,t,h)$ and $G^{\beta\gamma}(g,t,h)$, of the spectator and critical phases, respectively, which yields (4.32) with $\tilde{t}>0$. The extended triple line $\tilde{\tau}$ [see Figs. 1 and 4] is defined by $\tilde{h}=0$ for $\tilde{t}>0$, implying $y=0$. Since we consider only the vicinity of the extended triple line $\tilde{\tau}$, we must utilize the small y expansion (2.19) for the scaling function $W_+(y,y_4,y_5,\ldots)$ in (4.32). Using $\tilde{h}$ as the principle variable, which is advantageous in discussing the critical phase binodal, $\mathcal{B}^{\beta\gamma}$, the scaling function $W_+(y,y_4,y_5,\ldots)$ can be expanded in integral powers of $\tilde{h}$ with t-dependent coefficients. The noncritical function $D(g,t,h)$ can be expanded similarly. Then, solving (4.32) for $g_\sigma(t;\tilde{h})$ yields the desired nonsingular expansion. Here we consider only the leading t-dependent behavior of the resulting coefficients.

Accordingly, we rearrange (2.5) and (2.6) for $t>0$ using just the linear terms to obtain

$$h=\tilde{h}-r_{-1}t-r_0g+\cdots, \tag{4.63}$$

$$\tilde{t}=(1-q_0r_{-1})t+q_0\tilde{h}+(q_1-q_0r_0)g+\cdots. \tag{4.64}$$

The higher order terms in (2.5) and (2.6) enter only as correction terms in the t-dependent coefficients. The noncritical function $D(g,t,h)$ is then expanded, by recalling (2.2) and $D_e=0$, as

$$D(g,t,h)=(D_1-r_0D_3)g+(D_2-r_{-1}D_3)t+D_3\tilde{h}+\cdots. \tag{4.65}$$

Now we are in a position to find the isothermal boundary $g_\sigma(t;\tilde{h})$ above T_e.

In the *symmetric case*, we obtain

$$D_1g+D_2t+\cdots=-QW_{+0}^0|\tilde{t}|^{2-\alpha}-QW_{+2}^0U^2|\tilde{t}|^{-\gamma}\tilde{h}^2$$
$$+O(\tilde{h}^4). \tag{4.66}$$

By symmetry only even powers of $\tilde{h}$ appear. Solving for g with the aid of (4.64) then yields

$$g_\sigma(t;\tilde{h})=-g_{\sigma,0}^+t-g_{\sigma,1}^+t^{2-\alpha}-g_{\sigma,3}^+t^{-\gamma}\tilde{h}^2+\cdots, \tag{4.67}$$

where the coefficients are

$$g_{\sigma,0}^+=D_2/D_1,\quad g_{\sigma,1}^+=QD_1^{-3+\alpha}W_{+0}^0|D_1-q_1D_2|^{2-\alpha},$$
$$g_{\sigma,3}^+=QD_1^{\gamma-1}W_{+2}^0U^2|D_1-q_1D_2|^{-\gamma}. \tag{4.68}$$

Notice that the coefficient of the quadratic term in $\tilde{h}$ diverges as $T\to T_e+$. In terms of h, which is advantageous in deriving the spectator-phase binodal, $\mathcal{B}^\alpha$, we obtain the same leading t-dependent coefficients for $g_\sigma(t;h)$.

In the *nonsymmetric case*, terms linear in $\tilde{h}$ appear in the expansion of the scaling function $W_+(y,y_4,y_5,\ldots)$ arising from the odd $\boldsymbol{\kappa}$ exponents in (2.19). However, these terms only provide correction terms to the leading t-dependent behavior. Combining all the previous results yields the equation

$$(D_1-r_0D_3)g+(D_2-r_{-1}D_3)t+D_3\tilde{h}+\cdots$$
$$=-QW_{+0}^0|\tilde{t}|^{2-\alpha}-QW_{+2}^0U^2|\tilde{t}|^{-\gamma}\tilde{h}^2+\cdots. \tag{4.69}$$

Solving for g yields

$$g_\sigma(t;\tilde{h})=-g_{\sigma,0}^+t-g_{\sigma,1}^+t^{2-\alpha}-J_1\tilde{h}-g_{\sigma,3}^+t^{-\gamma}\tilde{h}^2+\cdots, \tag{4.70}$$

where J_1 is given above in (3.27) while the other coefficients are

$$g_{\sigma,0}^+=(D_2-r_{-1}D_3)/(D_1-r_0D_3),$$
$$g_{\sigma,1}^+=\frac{QW_{+0}^0}{(D_1-r_0D_3)}|\tilde{t}_\sigma|^{2-\alpha}, \tag{4.71}$$
$$g_{\sigma,3}^+=\frac{QW_{+2}^0U^2}{(D_1-r_0D_3)}|\tilde{t}_\sigma|^{-\gamma},$$

in which the numerical factor is

$$\tilde{t}_\sigma=(1-q_0r_{-1})-(q_1-q_0r_0)[(D_2-r_{-1}D_3)/(D_1-r_0D_3)]. \tag{4.72}$$

Notice, again, that the coefficient of the quadratic term in $\tilde{h}$ diverges when $T\to T_e+$. The result (4.70) can be expanded in terms of h by making the substitution

$$\tilde{h}=j_1h-r_{-1}t+\cdots, \tag{4.73}$$

where j_1 is given in (3.31). By utilizing (4.70), the coefficients $l_1,\ldots,\tilde{l}_2$ in (3.65) and (3.66) are found to be

$$\begin{aligned} l_1 &= 2(1-L_\sigma r_0)Q_e U^2 W^0_{+2}|\tilde{t}_\sigma|^{-\gamma}, \\ l_2 &= -\gamma(q_0-L_\sigma q_1)Q_e U^2 W^0_{+2}|\tilde{t}_\sigma|^{-\gamma-1}, \\ \tilde{l}_1 &= (2-\alpha)W^0_{+0}|\tilde{t}_\sigma|^{1-\alpha}\{[(q_5-2r_0q_6) \\ &\quad -2J_1(q_2-r_0q_5+r_0^2q_6)]Q_e \\ &\quad +(q_1-r_0q_0)[Q_3-J_1(Q_1-r_0Q_3)]\}, \\ \tilde{l}_2 &= -\gamma(q_1-r_0q_0)Q_e U^2 W^0_{+2}|\tilde{t}_\sigma|^{-\gamma-1}, \end{aligned} \tag{4.74}$$

where J_1 and $\tilde{t}_\sigma$ are defined in (3.27) and (4.72), respectively.

F. Spectator phase boundary: Isotherms below T_e

The spectator-phase boundary, $g_\sigma(t,h)$, below the endpoint temperature can be obtained as in the previous subsection by using the expansion (2.21) for the scaling function $W_-(y,y_4,\ldots)$ in (4.32). The $|y|$ factors in (2.21) yield the two branches of the phase boundary, $g_\sigma(t,h)$: see Figs. 2(a) and 5(a).

In the *symmetric case*, combining the results in Sec. IV E with the expansion (2.21) yields

$$\begin{aligned} D_1 g + D_2 t + \cdots &= -QW^0_{-0}|\tilde{t}|^{2-\alpha} - QW^0_{-1}U|\tilde{t}|^\beta|\tilde{h}| \\ &\quad - QW^0_{-2}U^2|\tilde{t}|^{-\gamma}\tilde{h}^2 + \cdots. \end{aligned} \tag{4.75}$$

Solving this for g with the aid of (4.64) provides the result,

$$\begin{aligned} g_\sigma(t;\tilde{h}) &= -g^-_{\sigma,0} - g^-_{\sigma,1}|t|^{2-\alpha} \mp g^-_{\sigma,2}|t|^\beta\tilde{h} - g^-_{\sigma,3}|t|^{-\gamma}\tilde{h}^2 \\ &\quad + \cdots, \end{aligned} \tag{4.76}$$

where the upper (lower) sign corresponds to $\tilde{h}>0$ (<0) while the coefficients are

$$\begin{aligned} g^-_{\sigma,0} &= D_2/D_1, \\ g^-_{\sigma,1} &= QD_1^{-3+\alpha}W^0_{-0}|D_1-q_1D_2|^{2-\alpha}, \\ g^-_{\sigma,2} &= QD_1^{-1-\beta}W^0_{-1}U|D_1-q_1D_2|^\beta, \\ g^-_{\sigma,3} &= QD_1^{\gamma-1}W^0_{-2}U^2|D_1-q_1D_2|^{-\gamma}. \end{aligned} \tag{4.77}$$

Notice that the linear term in $\tilde{h}$ vanishes as $T\to T_e-$, while the coefficient of the $\tilde{h}^2$ term diverges. In terms of h we obtain the same leading t-dependent coefficients for $g_\sigma(t;h)$.

Finally, in the *nonsymmetric case* we obtain the equation

$$\begin{aligned} &(D_1-r_0D_3)g + (D_2-r_{-1}D_3)t + D_3\tilde{h} + \cdots \\ &= -QW^0_{-0}|\tilde{t}|^{2-\alpha} - QW^0_{-1}U|\tilde{t}|^\beta|\tilde{h}| - QW^0_{-2}U^2|\tilde{t}|^{-\gamma}\tilde{h}^2 \\ &\quad + \cdots. \end{aligned} \tag{4.78}$$

By using (4.64), we can solve this for g to obtain

$$\begin{aligned} g_\sigma(t;\tilde{h}) &= -g^-_{\sigma,0}t - g^-_{\sigma,1}|t|^{2-\alpha} - (J_1 \pm g^-_{\sigma,2}|t|^\beta)\tilde{h} \\ &\quad - g^-_{\sigma,3}|t|^{-\gamma}\tilde{h}^2 + \cdots, \end{aligned} \tag{4.79}$$

where, again, the upper (lower) sign corresponds to $\tilde{h}>0$ (<0), while the coefficients are

$$\begin{aligned} g^-_{\sigma,0} &= \frac{(D_2-r_{-1}D_3)}{(D_1-r_0D_3)}, \quad g^-_{\sigma,1} = \frac{QW^0_{-0}}{(D_1-r_0D_3)}|\tilde{t}_\sigma|^{2-\alpha}, \\ g^-_{\sigma,2} &= \frac{QW^0_{-1}U}{(D_1-r_0D_3)}|\tilde{t}_\sigma|^\beta, \quad g^-_{\sigma,3} = \frac{QW^0_{-2}U^2}{(D_1-r_0D_3)}|\tilde{t}_\sigma|^{-\gamma}. \end{aligned} \tag{4.80}$$

Notice that the linear term in $\tilde{h}$ does not vanish in the *nonsymmetric case*, but the slopes of the two branches approach the same value as $T\to T_e-$. The coefficient of the quadratic term in $\tilde{h}$ diverges as the endpoint temperature is approached from below. As before the result (4.79) can be expressed in terms of h by using (4.73).

V. CONCLUSIONS

In summary, following earlier studies[8,9] stimulated by Widom,[9] we have investigated the singular shapes of the various isothermal binodals, or two-phase coexistence curves, in the density plane near a critical endpoint. However, whereas the previous studies assumed classical or van der Waals expressions for the critical thermodynamics, our work is based on *nonclassical* phenomenological scaling postulates set out, in Sec. II, in a general form encompassing a spectrum of correction-to-scaling variables. Four types of critical endpoints were distinguished and examined in detail: *nonsymmetric*, labeled **NA** or **NB** depending on whether the lambda-line $T_\lambda(g)$, which terminates at the endpoint (g_e,T_e), lies, **A**, below $T=T_e$ (as in Fig. 1) or, **B**, runs above (as in Fig. 4); and *symmetric*, labeled, correspondingly, **SA** and **SB**: see Fig. 4. At the endpoints, the lambda-line binodals $\mathcal{B}_e^{\lambda+}$ and $\mathcal{B}_e^{\lambda-}$ [see Fig. 6(b)] were found to be singular with a leading ''renormalized'' exponent $(1-\alpha)/\beta$ and subdominant singular correction exponents. The symmetric λ binodals are displayed in (3.10) [with explicit amplitude expressions recorded in (4.26)–(4.27)]; the nonsymmetric λ binodals are presented in (3.17).

Then, the *noncritical* or spectator-phase endpoint binodals $\mathcal{B}_e^{\alpha+}$ and $\mathcal{B}_e^{\alpha-}$ [see Figs. 3(b) and 6(b)] were found to be singular with a leading exponent $(\delta+1)/\delta$ (as conjectured by Widom[9]); the symmetric binodals are given in (3.36) with the closely spaced sequence of correction exponents listed in (3.38). The nonsymmetric binodals are similar but more complicated: see (3.44)–(3.49). The endpoint binodals $\mathcal{B}_e^\beta$ and $\mathcal{B}_e^\gamma$ which limit the critical phases [see Figs. 3(c) and 6(c)][21] have also been studied and were found to have the same leading exponent, $(1-\alpha)/\beta$, as the lambda-line binodals; the symmetric forms are given in (3.52), and the nonsymmetric expressions are in (3.56).

In addition, *above* the endpoint temperature the binodals separating the spectator-phase from the near-critical phase [see $\mathcal{B}^\alpha$ and $\mathcal{B}^{\beta\gamma}$ in Figs. 3(c) and 6(c)][21] were studied. They are analytic, but their slopes and curvatures develop singularities as $T\to T_e+$. The spectator-phase binodal is given in (3.58) and (3.59); its curvature diverges like $(T-T_e)^{-\gamma}$ when the critical endpoint is approached. The conjugate, near-critical-phase binodal is described by (3.64) and (3.67);

but in this case both the slope and the curvature *vanish*, although in singular fashion, upon approaching the endpoint.

Finally, the binodals that approach the three-phase region below the endpoint temperature have been considered. The spectator-phase binodals $\mathcal{B}_<^{\alpha-}$ and $\mathcal{B}_<^{\alpha+}$ [see Figs. 3(a) and 6(a)][21] are presented in (3.68) and (3.69); as above the endpoint, their curvatures both diverge when $T \to T_e$.

Our analysis has utilized certain essential convexity or thermodynamic stability properties at and near a critical endpoint and, for Ising-type criticality, also invoked a specific positivity of a scaling function expansion coefficient: see the discussion after Eqs. (2.20) and (2.24). These features are taken up in Ref. 17.

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[1] We use the terms thermodynamic *fields* and their conjugate *densities* in the sense carefully explained by R. B. Griffiths and J. C. Wheeler, Phys. Rev. A **2**, 1047 (1970); see also Ref. 2.

[2] M. E. Fisher and M. C. Barbosa, Phys. Rev. B **43**, 11 177 (1991); to be denoted **I** here. Equations from **I** will be written as **I**(3.2), etc. As far as practicable we adhere to the notation of **I**; however, a few details differ. In particular, we use h here in place of h_0 in **I** (and do not, in this analysis, utilize the analog of h in **I**).

[3] This suggestive terminology seems to be due to B. Widom, see, e.g., Chem. Soc. Rev. **14**, 121 (1985).

[4] M. E. Fisher and P. J. Upton, Phys. Rev. Lett. **65**, 2402 (1990); see also the Monte Carlo study by N. B. Wilding, *ibid.* **78**, 1488 (1997).

[5] See, e.g., the review by M. E. Fisher, in *Proceedings of the Gibbs Symposium*, edited by D. G. Caldi and G. D. Mostow (American Mathematical Society, Providence, Rhode Island, 1990), p. 39.

[6] M. C. Barbosa and M. E. Fisher, Phys. Rev. B **43**, 10 635 (1991); M. C. Barbosa, Physica A **177**, 153 (1991); Phys. Rev. B **45**, 5199 (1992).

[7] But note the comments below, after Eq. (2.6), regarding the Yang–Yang anomaly and "pressure mixing."

[8] C. Borzi, Physica A **133**, 302 (1985).

[9] D. Klinger, Chem. Phys. Lett. **145**, 219 (1988).

[10] J. H. Chen, M. E. Fisher, and B. G. Nickel, Phys. Rev. Lett. **48**, 630 (1982); but see also R. Guida and J. Zinn-Justin, J. Phys. A: Math. Gen. **31**, 8103 (1998) which may lead one to prefer the estimate $\theta_4 = 0.52 \pm 0.02$.

[11] Note that $d=4$ is a marginal dimensionality for simple critical behavior; thus this reduction as $d \to 4$ is only formal. In fact, one should anticipate logarithmic factors accompanying the 4/3 power of the noncritical binodal when $d=4$.

[12] M. E. Fisher, Phys. Rev. **176**, 257 (1968).

[13] In renormalization group language we are thus supposing that no "resonances" of eigenexponents arise, at least to the orders of interest. Such resonances may lead to logarithmic factors. However, for most applications in $d=3$ dimensions no such difficulties should be anticipated.

[14] M. E. Fisher and G. Orkoulas, Phys. Rev. Lett. **85**, 696 (2000).

[15] G. Orkoulas, M. E. Fisher, and C. Üstün, J. Chem. Phys. **113**, 7530 (2000).

[16] It can be seen that pressure-mixing will not alter the leading behavior of the various binodals, etc., but will enter the correction terms in various thermodynamic quantities.

[17] M. E. Fisher and Y. C. Kim (in preparation).

[18] F. H. A. Schreinemakers, in *Die Heterogen Gleichwichte vom Standpunkte der Phasenlehre*, edited by H. W. B. Roozeboom (Vieweg und Sohn, Braunschweig, 1913), Vol. III, Part 1, pp. 68–270.

[19] See also J. C. Wheeler, J. Chem. Phys. **61**, 4474 (1974); Phys. Rev. A **12**, 267 (1975); M. Teubner, J. Chem. Phys. **94**, 4490 (1991); **95**, 5243 (1991); **96**, 555 (1992).

[20] Note that, if L_σ and L_ρ should be infinite, we may merely interchange the labels of the g and h fields. Similarly, to place the β phase within the positive $(m, \tilde{m})$ quadrant the signs ascribed to the fields g and h may be appropriately adjusted.

[21] It should, perhaps, be emphasized that Figs. 2, 3, 5, and 6 are *qualitative* portrayals of the phase diagrams designed to bring out the principal significant features but are not quantitative representations of specific model free energies corresponding to Figs. 1 and 4, respectively.