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Bulk singularities at critical end points: a field-theory analysis

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Abstract. A class of continuum models with a critical end point is considered whose Hamiltonian $\mathcal{H}[\phi,\psi]$ involves two densities: a primary order-parameter field, ϕ, and a secondary (noncritical) one, ψ. Field-theoretic methods (renormalization group results in conjunction with functional methods) are used to give a systematic derivation of singularities occurring at critical end points. Specifically, the thermal singularity $\sim |t|^{2-\alpha}$ of the first-order line on which the disordered or ordered phase coexists with the noncritical spectator phase, and the coexistence singularity $\sim |t|^{1-\alpha}$ or $\sim |t|^{\beta}$ of the secondary density $\langle\psi\rangle$ are derived. It is clarified how the renormalization group (RG) scenario found in position-space RG calculations, in which the critical end point and the critical line are mapped onto two separate fixed points $\mathcal{P}^*_{\rm CEP}$ and $\mathcal{P}^*_{\lambda}$, translates into field theory. The critical RG eigenexponents of $\mathcal{P}^*_{\rm CEP}$ and $\mathcal{P}^*_{\lambda}$ are shown to match. $\mathcal{P}^*_{\rm CEP}$ is demonstrated to have a discontinuity eigenperturbation (with eigenvalue $y = d$), tangent to the unstable trajectory that emanates from $\mathcal{P}^*_{\rm CEP}$ and leads to $\mathcal{P}^*_{\lambda}$. The nature and origin of this eigenperturbation as well as the role redundant operators play are elucidated. The results validate that the critical behavior at the end point is the same as on the critical line.

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1 Introduction

Critical end points are widespread in nature. They occur when a line of critical temperatures (or lambda line) $T_{\rm c}(g)$, depending on a nonordering field g such as chemical potential or pressure, terminates at a line $g_\sigma(T)$ of discontinuous phase transitions [1–4]. In the past decades plenty of experimental and theoretical studies have been made in which critical end points were encountered [2–30]. Yet they have been rarely investigated for their own sake. This may be due to the physically appealing and widely accepted, though seldom carefully checked, expectation that the critical phenomena at such an end point should not differ in any significant way from critical phenomena along the critical line $T_{\rm c}(g)$ [2].

However, Fisher and collaborators have pointed out recently [3,5,10,11] that even the *bulk thermodynamics* of a critical end point should display new critical singularities, not observable on the critical line. For concreteness, let us consider the simple critical end point situation depicted in Figure 1 of a binary fluid mixture, whose critical line, λ,[1] is restricted to values $g \geq g_{\rm e}$ and ends at the end point temperature $T_{\rm e} = T_{\rm c}(g_{\rm e})$. We assume that the critical heat singularity at constant $g > g_{\rm e}$ on the critical line can be written as $A_{\pm}(g)\ |T - T_{\rm c}(g)|^{-\alpha}$, where $\alpha > 0$ in $d < 4$ dimensions. Fisher's assertion then is that the first-order phase boundary should vary as

$$g_\sigma(T) \approx g_\sigma^{\rm reg}(T) - \frac{X^0_{\pm}}{(2-\alpha)(1-\alpha)}\ |t|^{2-\alpha} \qquad (1)$$

as $t \equiv (T - T_{\rm e})/T_{\rm e} \to \pm 0$. Here $g_\sigma^{\rm reg}(T)$ is a regular background term, and X^0_+/X^0_- should be equal to the universal (and hence g independent) ratio A_+/A_-.

Equation (1) has been derived by using general thermodynamic arguments in conjunction with the phenomenological theory of scaling [3,5,10]. A straightforward extension of such reasoning reveals that the thermodynamic density conjugate to g, which in the present case can be identified as the total particle density $\varrho_{\rm tot}$, displays nonanalytic behavior of the form

$$\varrho^{\rm sing}_{\rm tot} \equiv \varrho_{\rm tot} - \varrho^{\rm reg}_{\rm tot}(T) \approx U^0_{\pm}\ |t|^{\beta} + V^0_{\pm}\ |t|^{1-\alpha} \qquad (2)$$

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[1] For the sake of simplicity, we shall henceforth refer to the critical line λ briefly as the 'λ-line', a term usually reserved for the critical line of normalfluid-to-superfluid transitions of He. Since we shall explicitly consider only the case of a scalar order parameter ϕ (even though parts of our analysis can be generalized in a straightforward fashion to more general cases with an multi-component order parameter), no confusion should arise from this slight abuse of terminology.

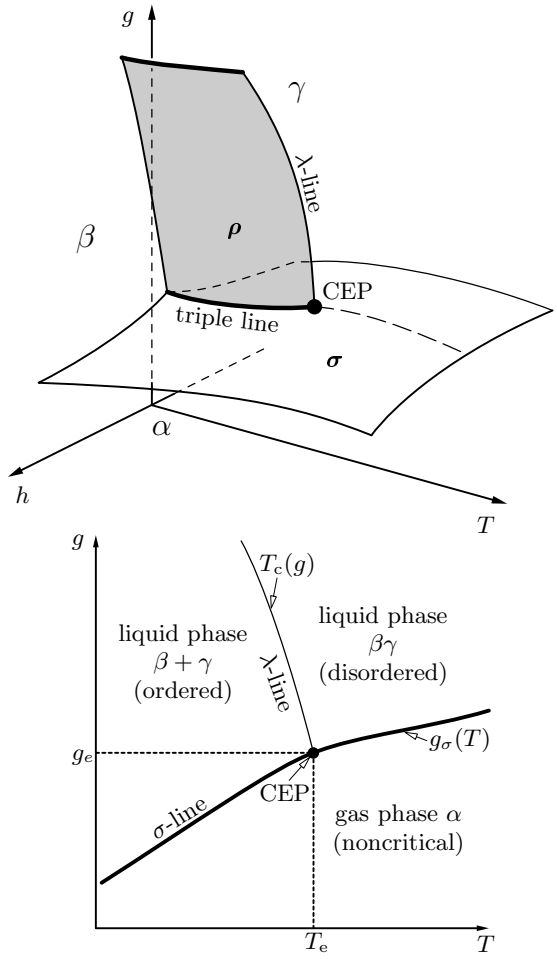

Fig. 1. Upper drawing: Schematic phase diagram showing, in a field space, portions of the coexistence surfaces $\boldsymbol{\rho}$ and $\boldsymbol{\sigma}$ for a nonsymmetric binary mixture with a liquid-liquid critical line λ and a critical end point CEP (full circle). The lower drawing represents the projection of the phase diagram on the gT-plane. Along the triple line the ordered phases β (A-rich) and γ (A-poor) coexist with the spectator phase α (vapor).

as the end point is approached along the liquid side of the liquid-vapor coexistence curve from $t > 0$ or $t < 0$ [13,14]. Here $\varrho_{\rm tot}^{\rm reg}(T)$ is regular at $T_{\rm e}$. Further, the amplitude $U_{\pm}^{0}$ vanishes for symmetric binary fluids whose properties are invariant with regard to simultaneous interchange of the two constituents A and B and their respective chemical potentials $\mu_{\rm A}$ and $\mu_{\rm B}$.

The $|t|^{2-\alpha}$ singularity of (1) has been confirmed for exactly solvable spherical models [16] and checked by Monte Carlo calculations [13,14]; the $|t|^{1-\alpha}$ singularity of (2) is consistent with the jump in the slope of $\varrho_{\rm tot}(T)$ found in mean field and density functional calculations [19,31] and has also been seen in Monte Carlo simulations [13–15].

Despite these advances the present state of the theory is anything but satisfactory. As can be seen from the thorough discussion given in reference [3], a number of challenging problems exist. First, a systematic derivation of the above-mentioned singularities within the framework of the modern field-theoretic renormalization group (RG) approach is lacking. We are aware of only a single field-theoretic analysis of critical end-point behavior that goes beyond Landau theory: the $(\epsilon = 4 - d)$-expansion study of a scalar ϕ^8 model with a negative ϕ^6 term by Ziman *et al.* [8]. In their one-loop calculation they found that both the critical line and the end point were controlled by the same, standard $O(\epsilon)$ fixed point. However, this model has very special properties: The first-order phase boundary does *not* extend into the disordered phase; as the critical end point is approached from the disordered phase, the order parameter $\langle\phi\rangle$ becomes critical *and* exhibits a jump to a nonvanishing value upon entering the ordered phase; no critical fluctuations occur in the ordered phase. Thus the model clearly does not reflect the typical critical end point situation in which the two-phase coexistence surface $\boldsymbol{\rho}$ bounded by the critical line $T_{\rm c}(g)$ meets the spectator phase boundary $\boldsymbol{\sigma}$ in a triple line (see Fig. 1).

Second, the above RG scenario for critical end points clearly differs from the one encountered in position-space RG analyses of lattice models [22,25]. These yielded the RG flow pattern depicted in Figure 2, in which the critical line is mapped onto the fixed point $\mathcal{P}_\lambda^*$, while the critical end point is described by a separate fixed point $\mathcal{P}_{\rm CEP}^*$. Since separate critical fixed points normally represent *distinct universality classes* of critical behavior, it would be natural to expect that the corresponding critical RG eigenexponents $y_t = 1/\nu$ and $y_h = \Delta/\nu$ take on *different values* at these fixed points. In reference [22,25] these values were found to match. Further, $\mathcal{P}_{\rm CEP}^*$ was found to involve an additional relevant eigenvector with eigenexponent $y = d$, characteristic of a discontinuity fixed point [32].

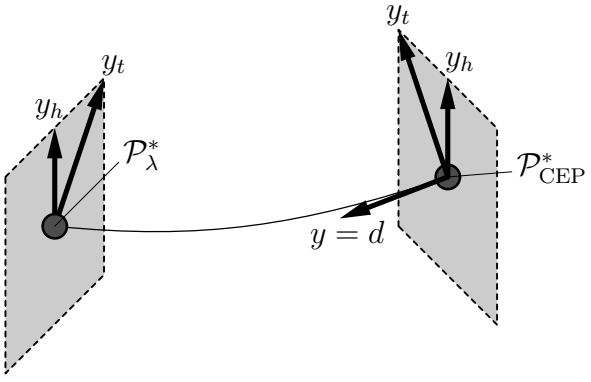

Fig. 2. Schematic RG flow pattern found for critical end points in position-space RG calculations [22,25]. The fixed point $\mathcal{P}_{\rm CEP}^*$, representing the critical end point, has two relevant eigenperturbations whose eigenexponents match those of the fixed point $\mathcal{P}_\lambda^*$, and a discontinuity eigenperturbation along the trajectory connecting the two fixed points, with eigenexponent $y = d$.

Whether this RG scenario – two separate fixed points $\mathcal{P}_\lambda^*$ and $\mathcal{P}_{\rm CEP}^*$ with matching critical spectra – is correct, remains to be seen. According to Fisher and Barbosa [3], it need not be the invariable rule, even though it should

normally be expected. If the latter is true, then one ought to be able to corroborate this RG scenario by means of a systematic derivation based on the field-theoretic RG approach. This should also yield a discontinuity eigenexponent at $\mathcal{P}^*_{\rm CEP}$, which the field-theoretic analysis of Ziman *et al.* [8] was unable to give.

A natural way to tackle this problem is to consider models involving *two* fluctuating densities, namely, a (primary) order parameter field ϕ and a secondary (noncritical) density ψ. The reason should be clear: Across $\boldsymbol{\rho}$, the order parameter has a jump singularity, but across $\boldsymbol{\sigma}$, another density – the thermodynamic density conjugate to g – is discontinuous. Obviously, a proper thermodynamic description requires *two* thermodynamic densities, in addition to the thermodynamic field T. Models of this sort have been investigated by means of Landau and density functional theory [18–20,31], and by Monte Carlo calculations [15]. Unless long-range interactions have been included also, they may be viewed as continuum versions of the Blume-Emery-Griffiths (BEG) model [33].

The continuum models with short-range interactions we shall consider here are of this kind but more general than the previously studied ones. They have been chosen in such a way that they can also be used to investigate interfacial critical phenomena such as the critical adsorption of one of the two components of the fluid at the interface between the liquid $\beta\gamma$ phase and the spectator phase α [34–37].

In the present paper[2] we shall confine our attention to *bulk* properties, leaving the study of critical adsorption, with the challenging question of whether the spectator phase α may be replaced by a hard wall (the 'wall assumption' of reference [11], implicit in virtually all work on critical adsorption at interfaces), to a forthcoming paper [40].

Our principal aims are the following. First, using field-theoretic means, we wish to give a systematic derivation of the coexistence singularities (1) and (2) *beyond the level of Landau theory*. Our second goal is to show that the critical behavior at the critical end point is the same as along the critical line λ, inasmuch as universal properties are concerned. To this end we shall have to clarify whether the RG flow pattern found in position-space RG calculation [22,25] prevails in our field-theoretic analysis. In particular, we shall verify the appearance of a g-dependent scaling field with RG eigenexponent $y = d$, and explain its origin and significance (*cf.* Ref. [38]).

An outline of the paper is as follows. In the next section, we introduce appropriate continuum models both for the case of symmetric and of nonsymmetric binary fluids; we justify their choice on the basis of phenomenological arguments, and show that they can be obtained from the BEG model by means of a Kac-Hubbard-Stratonovich transformation and subsequent continuum approximation. In Section 3, we utilize the Landau approximation to analyze these models; we verify that for suitable choices of their parameters, phase diagrams with the correct qualitative features result, determine the Landau-theory analogs of the coexistence singularities (1) and (2), and work out a number of perturbative results that will be needed in later sections. The field-theoretical analysis beyond Landau theory is taken up in Section 4. Section 5 summarizes our main results and conclusions. Finally, the Appendix contains some details of the mapping of the BEG model to the employed continuum models.

[2] A brief report of parts of the results presented here has been given in reference [38]; see also reference [39].

2 Models

2.1 Phenomenological considerations

The models we wish to consider have a Hamiltonian of the form

$$\mathcal{H}[\phi,\psi] = \mathcal{H}_1[\phi] + \mathcal{H}_2[\psi] + \mathcal{H}_{12}[\phi,\psi] \;, \tag{3}$$

where $\phi(\boldsymbol{x})$ and $\psi(\boldsymbol{x})$ are scalar fields on a bounded region Ω of the d-dimensional Euclidean space $\mathbb{R}^d$. It is understood that the limit $\Omega \uparrow \mathbb{R}^d$ is taken; since we shall only be concerned with bulk properties in the present paper, one can imagine Ω to be a d-dimensional hypercube with periodic boundary conditions whose linear extension is infinite. While ϕ, the primary order parameter field, becomes critical, the secondary field, ψ, is noncritical[3].

To simplify matters, we shall ignore long-range interactions. In real binary fluids, long-range interactions of the van der Waals' type are normally present. While these play a crucial role for – and would have to be included in a study of – wetting phenomena [41], they can be trusted to be irrelevant in the RG sense for critical phenomena. Anticipating that a gradient expansion be made, we presume that the Hamiltonian is a local functional depending on ϕ, ψ, and their gradients.

Consider first the case of a hypothetical binary fluid whose properties are *symmetric* with regard to interchange of the two constituents $\varsigma = \mathrm{A}, \mathrm{B}$. If the interaction between ς and ς' particles is described by a pair potential $U_{\varsigma\varsigma'}(\boldsymbol{r})$, then this symmetry is realized if $U_{\rm AA} = U_{\rm BB}$ and $\mu_{\rm A} = \mu_{\rm B}$, where $\mu_{\rm A,B}$ are the respective chemical potentials. For such symmetric binary fluids, one can identify ϕ and ψ (up to convenient normalization factors) with the difference $\varrho_{\rm A} - \varrho_{\rm B}$ and sum $\varrho_{\rm A} - \varrho_{\rm B}$ of the total local mass densities $\varrho_{\rm A,B}$, respectively. The Hamiltonian must be even in ϕ; that is, $\mathcal{H}$, $\mathcal{H}_1$, and $\mathcal{H}_{12}$ must satisfy the condition

$$\mathcal{H}[-\phi,\psi] = \mathcal{H}[\phi,\psi] \;. \tag{4}$$

On the other hand, terms even *and* odd in ψ are allowed.

[3] The term "noncritical" is not meant to imply that the correlation functions of the ψ field do not display any critical singularities. Owing to the coupling between between ψ and ϕ, correlation functions of the ψ field also display critical behavior, as should be clear and will be shown explicitly below. Only if this coupling vanishes, are the correlation functions of ψ those of a massive field theory.

Table 1. Canonical momentum dimensions for $d = 4 - \epsilon$.

ϕ	ψ	a_2	a_4	h	A	B
$1 - \frac{\epsilon}{2}$	$2 - \frac{\epsilon}{2}$	2	ϵ	$3 - \frac{\epsilon}{2}$	0	-2
b_2	b_4	g	d_{11}	d_{21}	e_{11}	e_{21}, f_{21}
0	$\epsilon - 4$	$2 - \frac{\epsilon}{2}$	1	$\frac{\epsilon}{2}$	-1	$\frac{\epsilon}{2} - 2$

We shall keep in $\mathcal{H}_1$ monomials up to fourth order in ϕ, in $\mathcal{H}_2$ those to the same order in ψ, and in $\mathcal{H}_{12}$ terms up to order $\phi^2\psi$. Further, contributions of higher than second order in the gradient operator ∇ will be discarded. It is convenient to make an $\boldsymbol{x}$-independent shift

$$\psi(\boldsymbol{x}) \to \psi(\boldsymbol{x}) + \Psi, \tag{5}$$

choosing Ψ such that the coefficient of the ψ^3 term in $\mathcal{H}_2$ vanishes. The requirement of invariance under the Euclidean group $\mathbb{E}(d)$ gives further restrictions, forbidding, in particular, terms linear in ∇ such as $\int_\Omega (\phi\nabla\psi - \psi\nabla\phi)$. Noting that $\int_\Omega \psi\Delta\phi^2$ equals $\int_\Omega \phi^2\Delta\psi$ up to boundary terms, we arrive at

$$\mathcal{H}_1[\phi] = \int_\Omega \left[\frac{A}{2}\,(\nabla\phi)^2 + \frac{a_2}{2}\,\phi^2 + \frac{a_4}{4}\,\phi^4 - h\phi\right], \tag{6}$$

$$\mathcal{H}_2[\psi] = \int_\Omega \left[\frac{B}{2}\,(\nabla\psi)^2 + \frac{b_2}{2}\,\psi^2 + \frac{b_4}{4}\,\psi^4 - g\psi\right], \tag{7}$$

and

$$\mathcal{H}_{12}[\phi,\psi] = \int_\Omega \left[d_{11}\,\phi\,\psi + \frac{d_{21}}{2}\,\phi^2\,\psi + e_{11}\,\phi\,\Delta\psi + \frac{e_{21}}{2}\,\phi^2\,\Delta\psi + \frac{f_{21}}{2}\,(\nabla\phi)^2\,\psi\right] \tag{8}$$

with

$$h = d_{11} = e_{11} = 0. \tag{9}$$

At the Gaussian fixed point at which ϕ is critical while ψ is noncritical, the coefficient a_2 vanishes, but b_2 remains nonzero. Since the coefficients A and b_2 could be transformed into unity by a change of normalization of ϕ and ψ, it is appropriate to take A and b_2 as dimensionless [42]. The momentum dimensions of the other parameters are listed in Table 1.

If the restriction $\mu_\mathrm{A} = \mu_\mathrm{B}$ is lifted by turning on a chemical potential difference $\mu_- = \mu_\mathrm{A} - \mu_\mathrm{B}$ while the AB-symmetry of the microscopic interactions persists, then property (4) will be lost, the interaction constants in (9) will no longer vanish, and a ϕ^3 term is to be expected in $\mathcal{H}_1$. The latter can be transformed away by making a shift

$$\phi(\boldsymbol{x}) \to \phi(\boldsymbol{x}) + \Phi, \tag{10}$$

analogous to (5). The coefficients of all contributions that are odd in ϕ must change sign as μ_- is reversed. This property carries over to Φ. Hence these interaction constants as well as Φ vary $\sim \mu_-$ for small μ_-.

In the general case, in which the interactions are not AB-symmetric, the interaction constants of the terms of $\mathcal{H}$ that break the $\phi \to -\phi$ symmetry are no longer odd in μ_- and hence do not vanish for $\mu_- = 0$. The same applies to the shift Φ. However, the Hamiltonian specified by (3) and (6–8) remains appropriate. The main difference is that the coefficients d_{11} and e_{11} do not vanish and we must consider nonzero values of the ordering field h.

Our choice of monomials retained in $\mathcal{H}[\phi,\psi]$ requires some comments. The ϕ-dependent part $\mathcal{H}_1$ is the standard ϕ^4 Hamiltonian, comprising all those monomials whose coefficients have nonnegative momentum dimensions for small $\epsilon = 4 - d \geq 0$ (*cf.* Tab. 1) and are not redundant (as is the ϕ^3 term) [43]. If besides $\mathcal{H}_1$ only the terms quadratic and linear in $\mathcal{H}_2$ and the one $\propto d_{21}$ in $\mathcal{H}_{12}$ were kept, then the Hamiltonian $\mathcal{H}$ would agree with the one utilized in the definition of the familiar dynamic model C [44].

The ψ^4 term with $b_4 > 0$ has been included for two reasons. First, if $b_2 < 0$, it is needed for stability. Second, we ought to be able to obtain a spectator phase boundary σ from our model. Therefore it is natural to require the model to yield such a coexistence surface already *in the absence of coupling to the primary field* ϕ (*i.e.*, for $\mathcal{H}_{12} = 0$). The obvious analog of $\boldsymbol{\sigma}$ for this case (and given $b_4 > 0$) is the plane $g = 0$; within Landau theory, the two (spectator and 'liquid') bulk phases coexisting there for $b_2 < 0$ correspond to the expectation values $\langle\psi\rangle = \pm\sqrt{|b_2|/b_4}$. Note that, rewritten in terms of the shifted and rescaled field

$$\psi_\pm = \sqrt{|b_2|}\left(\psi \mp \sqrt{\frac{|b_2|}{b_4}}\right), \tag{11}$$

$\mathcal{H}_2$ takes the form

$$\mathcal{H}_2[\psi] = \int_\Omega \left[\frac{B}{2|b_2|}\,(\nabla\psi_\pm)^2 + \psi_\pm^2 - g\,\psi_\pm \pm\sqrt{b_4}\,\psi_\pm^3 + \frac{b_4}{4}\,\psi_\pm^4 + \frac{1}{4b_4} \mp \frac{g}{\sqrt{b_4}}\right]. \tag{12}$$

Thus its $\psi_\pm^2$ term is positive and independent of b_4. The coefficients of the $\psi_\pm^3$ and $\psi_\pm^4$ terms in (12) (which have *negative* momentum dimensions) vanish as $b_4 \to 0$. If we let these coefficients as well as the one $\propto B$ of the $(\nabla\psi_\pm)^2$ monomial (whose momentum dimension is also negative) approach zero, and set the field g to the value $g = \pm 0$, then the $\psi_\pm$-dependent part of $\mathcal{H}_2$ turns into precisely this quadratic part, namely the Gaussian Hamiltonian

$$\mathcal{H}_\mathrm{G}[\psi_\pm] = \int_\Omega \psi_\pm^2. \tag{13}$$

For vanishing $\mathcal{H}_{12}$, this is a fixed-point Hamiltonian in the space of ψ-dependent Hamiltonians. We refrain from a more detailed discussion of RG issues here, reserving it to later sections. Note, however, that when the previously mentioned gradient, cubic, and quartic terms of $\mathcal{H}_2$ are dropped together with all contributions in $\mathcal{H}_{12}$ other than the one $\propto d_{21}$, then the total Hamiltonian $\mathcal{H}$ reduces to

the one of dynamic model C. A trivial, but useful, observation is that the constant part of the Hamiltonian (12) has a *g-dependent* part. Any constant in the integrand of a bulk Hamiltonian couples to $|\Omega| \equiv \int_\Omega$, the volume, and hence scales like a relevant scaling field with scaling index d under RG transformations. In Wegner's terminology [43], such a scaling field is called *special* rather than relevant, because of its well-known relationship with the analytic part of the bulk free energy density. In any case, we see already at this stage (where the coupling to the order parameter field ϕ has not yet been taken into account) a scaling field emerging that is odd in g and has scaling index d.

As stressed earlier, b_4 must not simply be set to zero: It must have a positive value in order that our model may yield a bulk phase diagram with the correct topology, for appropriate values of the other parameters (*cf.* Sect. 3). The coefficient B, on the other hand, can be set to zero in essentially all of our subsequent analysis. Our main reason for including this term is our intention of employing the model in a forthcoming paper [40] in a study of critical adsorption of binary fluid mixtures at their interface with the spectator gas phase. The coefficient B serves to provide a scale (correlation length) on which kink solutions $\check{\psi}_{-+}(z)$ of the Ginzburg-Landau equation for $\mathcal{H}_2$, connecting the asymptotic bulk solutions $\mp\sqrt{|b_2|/b_4}$ at $z = \pm\infty$, vary along the direction perpendicular to the interface. As $B \to 0$, these kinks become sharp steps. One does not need to be concerned about the vanishing of this scale here since we shall only deal with bulk properties below.

Likewise, the Laplacian terms $\propto e_{11}$ and $\propto e_{21}$ as well as the term $\propto f_{21}$ (all of which have *negative* momentum dimensions) have been introduced primarily with a view to our intended analysis of interfacial problems [40], and can be ignored in the sequel. However, the coupling term $\propto d_{11}$, which is also not present in the Hamiltonian of dynamic model C, must *not* be ignored in the general nonsymmetric case. As the reader might anticipate and will see below, it plays an important role in producing the $|t|^\beta$ part of the coexistence singularity (2).

2.2 Derivation from the Blume-Emery-Griffiths model

A familiar lattice model for binary mixtures that exhibits a critical end point is the BEG model [4,33]. This is a classical spin-1 lattice model with the Hamiltonian

$$\mathcal{H}_{\rm BEG}[\boldsymbol{S}] = -\sum_{\langle \boldsymbol{i},\boldsymbol{j}\rangle} \left[J\, S_{\boldsymbol{i}}\, S_{\boldsymbol{j}} + K\, S_{\boldsymbol{i}}^2\, S_{\boldsymbol{j}}^2 + L\left(S_{\boldsymbol{i}}^2\, S_{\boldsymbol{j}} + S_{\boldsymbol{i}}\, S_{\boldsymbol{j}}^2\right)\right] - \sum_{\boldsymbol{i}} \left(H\, S_{\boldsymbol{i}} + D\, S_{\boldsymbol{i}}^2\right), \quad S_{\boldsymbol{i}} = 0, \pm 1, \tag{14}$$

where $\langle \boldsymbol{i},\boldsymbol{j}\rangle$ indicates summation over nearest-neighbor pairs of lattice sites. Initially it was proposed to simulate ^{3}He-^{4}He mixtures; in this interpretation, a ^{3}He atom at site $\boldsymbol{i}$ corresponds to $S_{\boldsymbol{i}} = 0$ and a ^{4}He atom to $S_{\boldsymbol{i}} = \pm 1$ [33], so there is one and only one helium atom at each lattice site, and the model makes no allowance for vacancies.

However, the model may also be interpreted in a distinct – and for our purposes more appealing – fashion as a lattice-gas model for a binary fluid [45]. Then $\boldsymbol{i}$ is a label for microscopic cells that can hold at most a *single* A or B particle (atom or molecule), and the states $S_{\boldsymbol{i}} = +1$, -1, and 0 correspond, respectively, to the cases 'cell $\boldsymbol{i}$ is occupied by an A particle', 'cell $\boldsymbol{i}$ is occupied by a B particle', and 'cell $\boldsymbol{i}$ is empty'. Thus the variables H and D represent odd and even linear combinations of the chemical potentials $\mu_{\rm A}$ and $\mu_{\rm B}$ [45]:

$$H = \frac{\mu_{\rm A} - \mu_{\rm B}}{2\, k_{\rm B} T} \tag{15}$$

and

$$D = \frac{\mu_{\rm A} + \mu_{\rm B}}{2\, k_{\rm B} T}\,. \tag{16}$$

Without loss of generality, we can take $L > 0$ [45]. We also assume that $J > 0$ and $K > 0$. Thus, as J increases, the tendency for phase separation in the liquid state grows, and larger values of K correspond to a stronger drive of condensation of the mixture.

On sufficiently large length scales, the physics of the BEG model should be described by the continuum models introduced in the previous subsection. Hence one ought to be able to derive the latter from it. This may be achieved in much the same way as one can map the Ising model onto a continuum field theory, utilizing a Kac-Hubbard-Stratonovich transformation (see, *e.g.*, Ref. [46]). Details are given in the Appendix, where we show that the grand partition function of the BEG model,

$$\mathcal{Z}_{\rm BEG} = \sum_{\{S_{\boldsymbol{i}}=0,\pm 1\}} \mathrm{e}^{-\mathcal{H}_{\rm BEG}[S]}, \tag{17}$$

can we rewritten exactly as an integral over continuous fields $\phi_{\boldsymbol{i}}$ and $\psi_{\boldsymbol{i}}$, that is to say, as the partition function of a *lattice field theory*. One has

$$\mathcal{Z}_{\rm BEG} = \mathrm{e}^{-f_0(J,L,K)} \left[\prod_{\boldsymbol{i}} \int_{-\infty}^{+\infty} \mathrm{d}\phi_{\boldsymbol{i}} \int_{-\infty}^{+\infty} \mathrm{d}\psi_{\boldsymbol{i}}\right] \mathrm{e}^{-\mathcal{H}_{\rm lft}[\boldsymbol{\phi},\boldsymbol{\psi}]}. \tag{18}$$

The explicit form of this Hamiltonian $\mathcal{H}_{\rm lft}[\boldsymbol{\phi},\boldsymbol{\psi}]$ is given in (183) of the Appendix. As is shown there, making a continuum approximation then yields a Hamiltonian of the form specified by (3) and (6–8).

3 Landau theory

Landau theory is of value not only because of its simplicity and ability to reproduce essential topological features of the phase diagram, but also because it serves as the starting point of studies based on RG improved perturbation theory. Our main goal here is to convince ourselves that our model indeed yields a bulk phase diagram with a critical end point and the topology illustrated in Figure 1, providing the model parameters are in the appropriate range.

Since we shall only consider translationally invariant states here, we can take ϕ and ψ to be position-independent in the rest of this section. Hence all terms of $\mathcal{H}$ involving spatial derivatives do not contribute. If we drop these terms, then its part even in ϕ becomes equivalent to the Hamiltonian investigated in reference [19] *via* Landau theory. Thus, for the symmetric case, the results may be partly inferred from this reference.

In the Landau approximation, the grand potential (per volume and $k_{\mathrm{B}}T$) is given by

$$\mathcal{A}(a,b,d,h,g) = \inf_{\phi,\psi} \mathcal{V}(\phi,\psi), \tag{19}$$

with

$$\mathcal{V}(\phi,\psi) = \frac{1}{|\Omega|}\mathcal{H}[\phi,\psi], \tag{20}$$

where a, b, and d stand for the sets of parameters $\{a_2, a_4\}$, $\{b_2, b_4\}$, and $\{d_{11}, d_{21}\}$, respectively. From (6–8) we find

$$\mathcal{V}(\phi,\psi) = \frac{1}{2}\,(a_2 + d_{21}\,\psi)\,\phi^2 + \frac{a_4}{4}\,\phi^4 - h\phi + \frac{b_2}{2}\,\psi^2 + \frac{b_4}{4}\,\psi^4 + d_{11}\,\psi\phi - g\psi. \tag{21}$$

For the sake of thermodynamic stability, a_4 and b_4 are assumed to be positive.

In place of g we shall occasionally use the conjugate density

$$\check{\psi} \equiv -\left.\frac{\partial \mathcal{A}}{\partial g}\right|_{a,b,d,h} \tag{22}$$

as independent thermodynamic variable, utilizing the mixed field-density representation $(a,b,d,h,\check{\psi})$ instead of the field representation (a,b,d,h,g). The thermodynamic potential associated with the former is defined by

$$\mathcal{B}(a,b,d,h,\check{\psi}) = \inf_{\phi}\left\{\mathcal{V}(\phi,\check{\psi}) + g\check{\psi}\right\}. \tag{23}$$

3.1 Symmetric case

We first consider the symmetric case, setting $d_{11} = 0$. Owing to the implied invariance with regard to $(\phi,h) \to (-\phi,-h)$, we may restrict ourselves to values $h > 0$. Since a sign change of d_{21} can be compensated by simultaneous sign changes of ψ and g, we may furthermore presume that

$$d_{21} \le 0. \tag{24}$$

From the analysis presented in reference [19] it is clear that a variety of different types of phase diagrams (with critical points, critical end points, tricritical points, or special tricritical points) can be obtained, depending on the chosen range of the parameters a_2, b_2, d_{21}, and g. Our aim here is not to explore all these possibilities; rather we shall focus on the case of critical end points, and choose the values of these parameters accordingly.

The equilibrium densities must satisfy the (classical) equations of state

$$\frac{\partial \mathcal{V}(\phi,\psi)}{\partial \phi} = \frac{\partial \mathcal{V}(\phi,\psi)}{\partial \psi} = 0, \tag{25}$$

which in the present symmetric case become

$$(a_2 + d_{21}\,\psi)\,\phi + a_4\,\phi^3 = h, \tag{26}$$

$$b_2\,\psi + b_4\,\psi^3 + \frac{d_{21}}{2}\,\phi^2 = g. \tag{27}$$

From the $\phi \to -\phi$ symmetry (4) it is clear that the $\beta\gamma$ coexistence surface $\boldsymbol{\sigma}$ of the ordered ($\phi \neq 0$) states must lie in the $h = 0$ plane. Upon setting $h = 0$, the first equation of state, (27), can easily be solved for ϕ to determine that value $\phi_{\min}(\psi)$ at which $\mathcal{V}(\phi,\psi)$ becomes minimal for the given value of ψ. One finds

$$\phi_{\min}(\psi) = \begin{cases} 0\,, & \text{if } a_2 + d_{21}\,\psi > 0. \\ \pm\sqrt{\frac{|a_2 + d_{21}\,\psi|}{a_4}}\,, & \text{if } a_2 + d_{21}\,\psi < 0. \end{cases} \tag{28}$$

The critical value of ψ at which the bifurcation occurs,

$$\psi_\lambda = -\frac{a_2}{d_{21}}, \tag{29}$$

is the solution to

$$\frac{\partial^2}{\partial \phi^2}\,\mathcal{V}(0,\psi) = 0, \tag{30}$$

a condition that must be fulfilled whenever ϕ is critical at $\phi = 0$ and hence on the λ-line.

Upon inserting (28) into the right-hand side of (23), we obtain

$$\mathcal{B}(a,b,c,0,\psi) = \frac{b_2}{2}\,\psi^2 + \frac{b_4}{4}\,\psi^4 - \theta\!\left(a_2\,\frac{\psi - \psi_\lambda}{\psi_\lambda}\right)\frac{d_{21}^2}{4\,a_4}\,(\psi - \psi_\lambda)^2\,, \tag{31}$$

where $\theta(.)$ is the step function.

Since we wish the density ψ to be positive on the λ-line we take

$$a_2 \ge 0; \tag{32}$$

together with the inequality (24) this ensures that $\psi_\lambda > 0$. Under these conditions the trivial solution $\phi_{\min} = 0$ holds in the regime $\psi < \psi_\lambda$. Thus the equilibrium densities ψ_α and $\psi_{\beta\gamma}$ of the disordered vapor and liquid phases are solutions to the $\phi = 0$ analog of (27):

$$b_2\,\psi + b_4\,\psi^3 = g. \tag{33}$$

If $b_2 > 0$, there exists a unique real solution, which is positive or negative, depending on whether $g > 0$ or $g < 0$, namely

$$\eta_0(b_2,b_4,g) = \frac{1}{3}\,(r_0)^{1/3} - \frac{b_2}{b_4}\,(r_0)^{-1/3} \tag{34}$$

with

$$r_0 = \frac{27}{2}\,\frac{g}{b_4} + \sqrt{\frac{729}{4}\left(\frac{g}{b_4}\right)^2 + 27\left(\frac{b_2}{b_4}\right)^3}. \quad (35)$$

It has the power-series expansion

$$\eta_0(b_2 \geq 0, b_4, g) = \frac{g}{b_2} - \frac{b_4\, g^3}{b_2^4} + \frac{3\, b_4^2\, g^5}{b_2^7} + O\big(g^7\big), \quad (36)$$

where the subscript 0 is to remind us that the solution vanishes for $g = 0$. For $b_2 < 0$, (33) has three real solutions if

$$|g| < g_< \equiv \frac{2\,|b_2|^{3/2}}{3\sqrt{3\,b_4}}, \quad (37)$$

and a single real one if $|g| > g_<$. We denote the ones that turn in the limit $g \to 0$ into the nontrivial $g \neq 0$ solutions $\pm\sqrt{|b_2|/b_4}$ as $\eta_\pm(b_2, b_4, g)$. They have the property

$$\eta_-(b_2, b_4, g) = -\eta_+(b_2, b_4, -g) \quad (38)$$

and the power-series expansion

$$\eta_\pm(b_2 \leq 0, b_4, g) = \pm\sqrt{\frac{|b_2|}{b_4}} + \frac{g}{2\,|b_2|} \mp \frac{3\sqrt{b_4}\, g^2}{8\,|b_2|^{5/2}} + \frac{b_4\, g^3}{2\,|b_2|^4} \mp \frac{105\, b_4^{3/2} g^4}{128\,|b_2|^{11/2}} + \frac{3\, b_4^2\, g^5}{2\,|b_2|^7} + O\big(g^6\big). \quad (39)$$

Further, η_+ is given by the analog of the result (34) for η_0 one obtains through the replacement $b_2 \to -|b_2|$, both in (34) and the expression (35) for r_0.

In terms of these solutions, the densities of the *disordered fluid state* become

$$\phi = 0\,,\ \psi = \eta_0(b_2, b_4, g)\,,\ \text{ for } b_2 > 0\,,\ h = 0\,,\ \psi < \psi_\lambda, \quad (40)$$

while the densities of the *disordered vapor phase* α and the *disordered liquid phase* $\beta\gamma$ read

$$\begin{matrix}(\phi_\alpha, \psi_\alpha) \\ (\phi_{\beta\gamma}, \psi_{\beta\gamma})\end{matrix} \begin{matrix}= (0, \eta_-(b_2, b_4, g)) \\ = (0, \eta_+(b_2, b_4, g))\end{matrix} \quad \text{for} \quad \begin{cases} b_2 < 0\,, \\ h = 0\,, \\ \psi < \psi_\lambda. \end{cases} \quad (41)$$

In the latter two cases, the solutions η_+ ($\beta\gamma$ phase) and η_- (α phase) are the thermodynamic stable ones if $g > 0$ and $g < 0$, respectively; the remaining two real roots of (34) one has if $|g| < g_<$ correspond to metastable and unstable states.

At $g = 0$, these states coexist down to that value of b_2 at which $\psi_{\beta\gamma}$ intersects the line $\psi = \psi_\lambda$, which is

$$b_{2e} = -b_4\,\psi_\lambda^2 = -b_4\left(\frac{a_2}{d_{21}}\right)^2, \quad (42)$$

provided

$$\psi_\lambda > \frac{-d_{21}}{2\sqrt{a_4\, b_4}}\,\cdot \quad (43)$$

As we shall show below, this condition guarantees that no tricritical point appears. The resulting phase diagram is displayed in Figure 3 in a mixed field/density representation, and in Figure 4 in a field representation; it corresponds to case (e) of reference [19][4]. There is a liquid-vapor critical point at $b_2 = \psi = 0$ and a critical end point at $b_2 = b_{2e}$, $\psi = \psi_\lambda$. The boundaries of the α-$\beta\gamma$ coexistence region for $b_{2e} < b_2 < 0$ are given by the $g = 0$ solutions $\eta_\pm$ of (39).

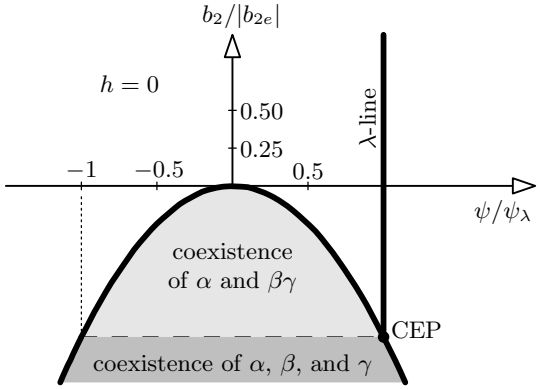

Fig. 3. Phase diagram of the symmetric model in the Landau approximation. The diagram is shown in a mixed field/density representation and corresponds to the following choice of parameter values: $a_2 = 5$, $a_4 = b_4 = 1/6$, $d_{21} = -1/2$, $d_{11} = 0$, giving $\psi_\lambda = 10$ and $b_{2e} = 50/3$.

In order to determine the boundaries of the region of coexistence of the α, β, and γ phases, one generally must resort to numerical methods. However, for $b_2 \lesssim b_{2e}$, the value g takes on the triple line, g_σ, is small, as is the order parameter ϕ for $\psi \gtrsim \psi_\lambda$ in the vicinity of the critical end point. This enables us to determine the phase boundaries in this regime in a perturbative manner. Note, first, that the equilibrium densities ψ_β and ψ_γ ($= \psi_\beta$ for $h = 0$) can be written in terms of

$$\psi_+(g) \equiv \eta_+(b_2, b_4, g) \quad (44)$$

and expanded as

$$\psi_{\beta,\gamma} = \eta_+\left(b_2, b_4, g - \frac{1}{2}\, d_{21}\, \phi_{\beta,\gamma}^2\right) \quad (45)$$

$$= \psi_+(g) - \psi_+{}'(g)\,\frac{d_{21}}{2}\,\phi_{\beta,\gamma}^2 + \psi_+{}''(g)\,\frac{d_{21}^2}{8}\,\phi_{\beta,\gamma}^4 + O\big(\phi_{\beta,\gamma}^6\big), \quad (46)$$

with

$$\psi_+{}'(g) = \big[3\, b_4\, \psi_+^2(g) - |b_2|\big]^{-1} \quad (47)$$

[4] In order to check the consistency with reference [19], one should identify the variables ϱ, a, μ and A utilized there with $-\psi$, a_2, $-g$, and b_2, respectively, and set $a_4{=}d_{21}{=}b_2{=}b_4{=}1$.

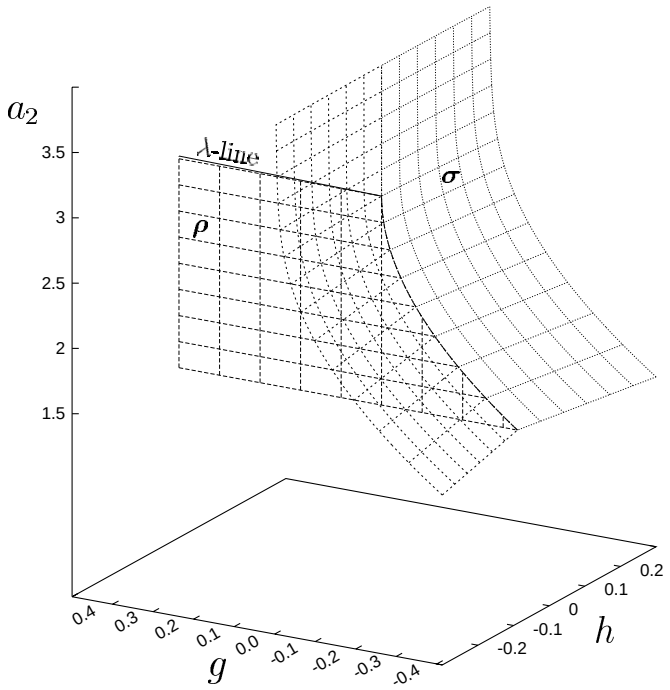

Fig. 4. The analog of Figure 3 in an a_2gh field representation, as obtained by solving the equations of Landau theory through numerical means. For b_2 we have chosen the value $b_2 = -6$; the remaining parameters have the same values as in Figure 3, *i.e.*, $a_4 = b_4 = 1/6$, $d_{21} = -1/2$, and $d_{11} = 0$. Only the neighborhood of the critical end point is shown.

and

$$\psi_+{}''(g) = -\frac{6\,b_4\,\psi_+(g)}{\left[3\,b_4\,\psi_+^2(g) - |b_2|\right]^3}. \tag{48}$$

Inserting the expansion (46) into the equation of state (26) with $h = 0$ gives

$$[a_2 + d_{21}\,\psi_+(g)]\,\phi + \left[a_4 - \frac{d_{21}^2}{2}\,\psi_+{}'(g)\right]\phi^3 + \frac{d_{21}^3}{8}\,\psi_+{}''(g)\,\phi^5 = O\left(\phi^7\right). \tag{49}$$

We seek nontrivial solutions of this equation for

$$\check{a}_2[\psi_+(g)] \equiv a_2 + d_{21}\,\psi_+(g) < 0\,. \tag{50}$$

If the coefficient of the ϕ^3 term in (49) is positive,

$$\check{a}_4[\psi_+(g)] \equiv a_4 - \frac{d_{21}^2}{2}\,\psi_+{}'(g) > 0, \tag{51}$$

then the equation (49) for ϕ can be solved in a straightforward manner to obtain

$$\phi_\beta = -\phi_\gamma = \sqrt{\frac{|\check{a}_2[\psi_+(g)]|}{\check{a}_4[\psi_+(g)]}}\;\left(1 + o[\check{a}_2(\psi_+)]\right), \tag{52}$$

giving

$$\psi_{\beta,\gamma} \approx \psi_+(g) - \psi_+{}'(g)\,\frac{d_{21}}{2}\,\frac{|\check{a}_2[\psi_+(g)]|}{\check{a}_4[\psi_+(g)]}\,. \tag{53}$$

The above analysis suggests that $\check{a}_4[\psi_+(g)]$ plays the role of an effective ϕ^4 interaction constant. To verify this one can calculate $d^4\mathcal{V}\big[\phi, \psi_{\beta,\gamma}(\phi)\big]/d\phi^4\big|_{\phi=0}$ along a path $\psi_{\beta,\gamma}(\phi)$, where $\psi_{\beta,\gamma}(\phi)$ is given by (45), with the replacement $\phi_{\beta,\gamma} \to \phi$. A straightforward calculation gives

$$\left.\frac{d^4\mathcal{V}\Big[\phi, \psi_{\min}^{(\beta,\gamma)}(\phi)\Big]}{d\phi^4}\right|_{\phi=0} = 6\,\check{a}_4[\psi_+(g)], \tag{54}$$

where the equation of state (26) and the results (47) and (48) for the derivatives of $\psi_+(g)$ were used. Hence (51) is the usual condition for the absence of a tricritical point at $\phi = 0$. At the critical end point it becomes

$$a_4 > \frac{d_{21}^2}{4\,|b_{2e}|} = \frac{1}{b_4}\left(\frac{d_{21}}{2\,\psi_\lambda}\right)^2, \tag{55}$$

which in turn implies our initially stated condition (43) if $d_{21} < 0$ and $\psi_\lambda > 0$, as assumed.

The location of the triple line, g_σ, can now be determined from the coexistence condition

$$\mathcal{A}_\alpha(a, b, d, 0, g_\sigma) = \mathcal{A}_{\beta,\gamma}(a, b, d, 0, g_\sigma) \tag{56}$$

for the grand potentials

$$\mathcal{A}_\wp(a, b, d, h, g) = \mathcal{V}(\phi_\wp, \psi_\wp)\;, \quad \wp = \alpha, \beta, \gamma. \tag{57}$$

Upon substituting the above results for $(\phi_{\beta,\gamma}, \psi_{\beta,\gamma})$ together with $(\phi_\alpha, \psi_\alpha)$ from (41) into the latter equation, the former one can be solved beneath the critical end point to obtain

$$g_\sigma = -\left\{\frac{[\check{a}_2(\psi)]^2}{8\,\check{a}_4(\psi)\,\psi} + O\Big([\check{a}_2(\psi)]^3\Big)\right\}_{\psi=\psi_+(0)} \tag{58}$$

$$= -\frac{\left(a_2 + d_{21}\sqrt{\frac{|b_2|}{b_4}}\right)^2}{8\left(a_4 - \frac{d_{21}^2}{4\,|b_2|}\right)\sqrt{\frac{|b_2|}{b_4}}} + O\big(\check{a}_2^3\big) \tag{59}$$

for $\check{a}_2\big[\sqrt{|b_2|/b_4}\big] = a_2 + d_{21}\sqrt{\frac{|b_2|}{b_4}} \lesssim 0$.

The latter quantity varies as $\check{a}_2 \approx a_{2,\pm}^0\,|t|$ near the critical end point, while the denominator in (58) approaches a nonvanishing constant there. Remembering that $g_\sigma = 0$ for $\check{a}_2 > 0$ (*i.e.*, $t > 0$), we arrive at

$$\left.\frac{\partial^2 g_\sigma(t)}{\partial t^2}\right|_{t=0\pm} = \begin{cases} 0 & \text{for } t = 0^+, \\ \frac{-\left(a_{2,-}^0\right)^2}{4\,\check{a}_{4e}\sqrt{|b_{2e}|/b_{4e}}} & \text{for } t = 0^-, \end{cases} \tag{60}$$

where the subscript e denotes values at the critical end point. Hence $\partial^2 g_\sigma/\partial t^2$ has indeed a jump singularity at the end point, as found in other analyses of the mean-field type [18–20,31] and is in conformity with the $\alpha = 0$ analog of the predicted singularity (1).

Likewise, the singularity[5] of the liquid ($\beta\gamma$ or β,γ) branch of the α-$\beta\gamma$ and α-β-γ coexistence regions,

$$\psi^{\rm sing}_{\beta\gamma/\beta,\gamma} \approx -\frac{d_{21,e}\,|a^0_{2,-}|}{4\,|b_{2e}|\,\check{a}_{4e}}\,|t|\,\theta(-t)\;, \tag{61}$$

resulting from the second term in (53) is the mean-field analog of the one $\sim |t|^{1-\alpha}$ in (2); it means that in Landau theory the first temperature derivative of $\psi_{\beta,\gamma}$ is *discontinuous* at the critical end point (*cf.* Refs. [13,14]).

The curve in which this portion of the coexistence boundary intersects the $b_2\psi$ plane – *i.e.*, the right branch of the liquid phase boundary in Figure 3, described by the mapping $b_2 \mapsto \psi_{\beta\gamma}$ and $b_2 \mapsto \psi_{\beta,\gamma}$ for $0 > b_2 > b_{2e}$ and $b_{2e} > b_2$, respectively, – also has a discontinuous slope at the end point. One finds

$$\left.\frac{\partial\psi_{\beta\gamma/\beta,\gamma}}{\partial b_2}\right|_{b_2=b_{2e}+0} = \frac{-|d_{21}|}{2\,a_2\,b_4} \tag{62}$$

and

$$\begin{aligned}\left.\frac{\partial\psi_{\beta\gamma/\beta,\gamma}}{\partial b_2}\right|_{b_2=b_{2e}-0} &= \frac{-|d_{21}|}{2\,a_2\,b_4} - \frac{|d_{21}|^5}{2\,a_2\,b_4\,(4\,a_2^2\,a_4\,b_4 - |d_{21}|^4)} \\ &= -\frac{2\,a_2\,a_4\,|d_{21}|}{4\,a_2^2\,a_4\,b_4 - |d_{21}|^4}.\end{aligned} \tag{63}$$

3.2 Nonsymmetric case

We now turn to the case of a nonsymmetric critical end point, assuming that $d_{11} > 0$. Owing to the implied explicit breaking of the $\phi \to -\phi$ symmetry, the coexistence surface $\boldsymbol{\rho}$ should neither be located in the $h = 0$ plane nor be parallel to it. Hence we must consider nonvanishing values of h from the outset. Instead of (26) and (27), the classical equations of state (25) now read

$$(a_2 + d_{21}\,\psi)\,\phi + d_{11}\,\psi + a_4\,\phi^3 = h, \tag{64}$$

$$b_2\,\psi + b_4\,\psi^3 + d_{11}\,\phi + \frac{d_{21}}{2}\,\phi^2 = g\;. \tag{65}$$

Using the solutions $\eta_{0,\pm}$ introduced in (34, 36), and (39), the former can be solved for ϕ to obtain

$$\phi = \eta_{0,\pm}(a_2 + d_{21}\,\psi, a_4, h - d_{11}\,\psi), \tag{66}$$

where the subscript 0 is to be taken whenever $a_2 + d_{21}\,\psi > 0$, while the choices $\pm$ apply to the cases $a_2 + d_{21}\,\psi < 0$ with $h - d_{11}\,\psi \gtrless 0$, respectively. Likewise, solving the other equation of state, (64), for ψ gives

$$\psi = \eta_{0,\pm}\left(b_2, b_4, g - d_{11}\,\phi - \frac{d_{21}}{2}\,\phi^2\right)\;. \tag{67}$$

[5] To obtain the leading temperature singularity given here, one may replace $g_\sigma(t)$ by its limiting value $g_e = g_\sigma(t=0)$; the $|t|^2$ singularity (60) of $g_\sigma(t)$ produces *subleading* nonanalytic contributions to $\psi_{\beta\gamma/\beta,\gamma}$.

Since we shall continue to take $b_2 < 0$, the subscripts $\pm$ are the appropriate choices, depending on whether

$$\check{g}(\phi) \equiv g - d_{11}\,\phi - (d_{21}/2)\,\phi^2 \tag{68}$$

is positive or negative.

From the above equations one can read off that the solutions $\phi_{\rm min}(\psi)$ given in (28) now apply on the hyperplane $h = d_{11}\,\psi$. If $a_2 + d_{21}\,\psi > 0$, then any thermodynamically stable state on this hyperplane must have $\phi = 0$. Furthermore, the liquid-gas critical point is seen to remain at $b = g = h = 0$.

Since ϕ_λ, the equilibrium value ϕ takes on the λ-line, generically does not vanish, the fields ϕ and ψ do no longer decouple there. To see this, let us compute the Hessian of $\mathcal{V}$,

$$\boldsymbol{\mathcal{V}}^{(2)}(\phi,\psi) \equiv \begin{pmatrix} \mathcal{V}_{\phi\phi} & \mathcal{V}_{\phi\psi} \\ \mathcal{V}_{\psi\phi} & \mathcal{V}_{\psi\psi} \end{pmatrix} = \begin{pmatrix} \frac{\partial^2\mathcal{V}}{\partial\phi\,\partial\phi} & \frac{\partial^2\mathcal{V}}{\partial\phi\,\partial\psi} \\ \frac{\partial^2\mathcal{V}}{\partial\phi\,\partial\psi} & \frac{\partial^2\mathcal{V}}{\partial\psi\,\partial\psi} \end{pmatrix}, \tag{69}$$

at a solution $\phi = \phi_{\rm cl}$, $\psi = \psi_{\rm cl}$ of the equations of state (64) and (65) ("classical solution"). This quantity is nothing but the Fourier transform

$$\tilde{\boldsymbol{\Gamma}}^{(2)}(\boldsymbol{q}) = \left(\int {\rm d}^d x_{12}\,\Gamma_{\mu\nu}(\boldsymbol{x}_1,\boldsymbol{x}_2;)\,{\rm e}^{{\rm i}\boldsymbol{q}\cdot\boldsymbol{x}_{12}}\right) \tag{70}$$

at momentum $\boldsymbol{q} = \boldsymbol{0}$ of the familiar Ornstein-Zernicke expression for the two-point vertex function

$$\Gamma_{\mu\nu}(\boldsymbol{x}_1,\boldsymbol{x}_2) \equiv \frac{\delta^2\Gamma[\phi{=}\phi_{\rm cl},\psi{=}\psi_{\rm cl}]}{\delta\mu(\boldsymbol{x}_1)\,\delta\nu(\boldsymbol{x}_2)}\;. \tag{71}$$

Here the indices μ, ν take the values ϕ, ψ. Further, $\boldsymbol{x}_{12}$ means the deplacement vector $\boldsymbol{x}_1 - \boldsymbol{x}_2$, and $\Gamma[\phi,\psi] = \mathcal{H}[\phi,\psi]$ in the Landau approximation used here.

As is borne out by the result

$$\boldsymbol{\mathcal{V}}^{(2)}(\phi_{\rm cl},\psi_{\rm cl}) = \begin{pmatrix} a_2 + d_{21}\,\psi_{\rm cl} + 3\,a_4\,\phi_{\rm cl}^2 & d_{11} + d_{21}\,\phi_{\rm cl} \\ d_{11} + d_{21}\,\phi_{\rm cl} & b_2 + 3\,b_4\,\psi_{\rm cl}^2 \end{pmatrix}, \tag{72}$$

the Hessian now is generically *nondiagonal*, even in the $\phi = 0$ plane (where it is diagonal in the symmetric case).

A principal axis transformation with the orthogonal transformation matrix

$$\boldsymbol{U} = \begin{pmatrix} \cos\vartheta & \sin\vartheta \\ -\sin\vartheta & \cos\vartheta \end{pmatrix} \tag{73}$$

yields the diagonal matrix

$${\rm diag}\,(\lambda_1,\lambda_2) = \boldsymbol{U}^{\rm T}\cdot\boldsymbol{\mathcal{V}}^{(2)}(\phi_{\rm cl},\psi_{\rm cl})\cdot\boldsymbol{U} \tag{74}$$

with the eigenvalues

$$\lambda_{\frac{1}{2}} = \frac{\mathcal{V}_{\phi\phi} + \mathcal{V}_{\psi\psi}}{2} \mp \frac{1}{2}\sqrt{(\mathcal{V}_{\psi\psi} - \mathcal{V}_{\phi\phi})^2 + 4\,\mathcal{V}_{\phi\psi}{}^2}\;, \tag{75}$$

where the angle ϑ is given by

$$\tan 2\vartheta = \frac{2\,\mathcal{V}_{\phi\psi}}{\mathcal{V}_{\psi\psi} - \mathcal{V}_{\phi\phi}}\,. \tag{76}$$

We write the associated eigendensities as

$$\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix} = \boldsymbol{U}^{\mathrm{T}}\cdot\begin{pmatrix}\phi-\phi_{\mathrm{cl}}\\ \psi-\psi_{\mathrm{cl}}\end{pmatrix}. \tag{77}$$

On the λ-line, the Hessian $\boldsymbol{\mathcal{V}}^{(2)}(\phi_\lambda,\psi_\lambda)$ must have one vanishing eigenvalue, λ_1, and a positive one, λ_2:

$$\lambda_1(\phi_\lambda,\psi_\lambda) = 0\,, \quad \lambda_2(\phi_\lambda,\psi_\lambda) > 0. \tag{78}$$

In order that $\mathcal{V}(\phi,\psi) > \mathcal{V}(\phi_\lambda,\psi_\lambda)$ for small deviations φ_1 with $\varphi_2 = 0$, the third derivative of $\mathcal{V}$ along the eigendirection φ_1,

$$\left.\frac{\partial^3\mathcal{V}}{\partial\varphi_1^3}\right|_{\mathrm{cl}} = 6\,a_4\,\phi_{\mathrm{cl}}\,\cos^3\vartheta - 3\,d_{21}\,\cos^2\vartheta\,\sin\vartheta - 6\,b_4\,\psi_{\mathrm{cl}}\,\sin^3\vartheta, \tag{79}$$

must vanish on the λ-line:

$$\left.\frac{\partial^3\mathcal{V}}{\partial\varphi_1^3}\right|_{\lambda} = 0, \tag{80}$$

while the corresponding fourth derivative

$$\left.\frac{\partial^4\mathcal{V}}{\partial\varphi_1^4}\right|_{\mathrm{cl}} = 6\,a_4\,\cos^4\vartheta + 6\,b_4\,\sin^4\vartheta \tag{81}$$

has to be positive there. The latter is guaranteed by our assumptions that $a_4 > 0$ and $b_4 > 0$.

Finally, the analog of the requirement (51) that the effective ϕ^4 coupling constant be positive becomes

$$\frac{1}{6}\left[\left.\frac{d^4}{d\varphi_1^4}\right|_{\varphi_2^{\min}(\varphi_1)}\mathcal{V}\right]_{\mathrm{cl}} \equiv \breve{a}_4(\phi_{\mathrm{cl}},\psi_{\mathrm{cl}}) > 0\,, \tag{82}$$

where the derivative on the left-hand side is along a path $\varphi_1 \mapsto \varphi_2^{\min}(\varphi_1)$ through $(\phi_{\mathrm{cl}},\psi_{\mathrm{cl}})$ on which φ_2 takes that value $\varphi_2^{\min}(\varphi_1)$ which minimizes $\mathcal{V}$ for given φ_1. Exploiting the fact that

$$\frac{\partial\mathcal{V}}{\partial\varphi_1}\,d\varphi_1 = -\frac{\partial\mathcal{V}}{\partial\varphi_2}\,d\varphi_2 \tag{83}$$

on this path, one is led to the result

$$\breve{a}_4(\phi_{\mathrm{cl}},\psi_{\mathrm{cl}}) = \left[\frac{1}{6}\,\frac{\partial^4\mathcal{V}}{\partial\varphi_1^4} - \frac{1}{2\,\lambda_2}\,\left(\frac{\partial^3\mathcal{V}}{\partial\varphi_1^3}\right)^2\right]_{\mathrm{cl}}, \tag{84}$$

which is compatible with, and generalizes, (51).

Let $a_{2\lambda}$ and h_λ be the values a_2 and h take as a function of g and the other variables on the λ-line. These values are fixed by the first one of the conditions (78), $\lambda_1 = 0$, and (80). To determine the coexistence surfaces $\boldsymbol{\rho}$ and $\boldsymbol{\sigma}$, one must again exploit the equality of the grand potentials of the corresponding coexisting phases [*cf.* (57)].

Since ϕ_λ now does no longer vanish, these conditions are not easy to handle analytically. In general, one must recourse to numerical methods. Figure 5 shows an example of a phase diagram obtained in this fashion for the choice of interaction constants given in the caption. As expected, the coexistence surface $\boldsymbol{\rho}$, and hence the critical end point, are displaced from the $h = 0$ plane. Further, $\boldsymbol{\rho}$ gets curved, and the reflection symmetry of the phase diagram with respect to $\boldsymbol{\rho}$ we had in the symmetric case is lost.

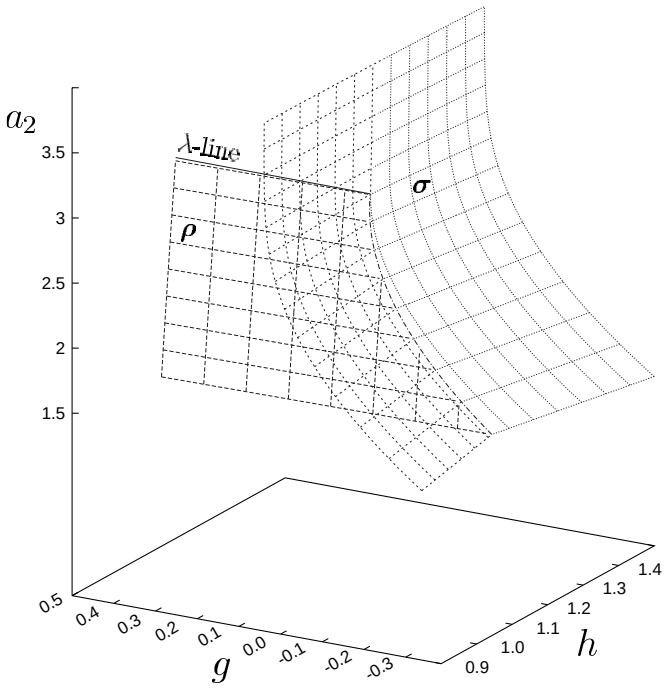

Fig. 5. Phase diagram of the nonsymmetric model in the Landau approximation. The results, obtained by numerical (and analytical, see text) solutions of the equations of state, correspond to the following choice of parameter values: $b_2 = -6$, $a_4 = b_4 = 1/6$, $d_{21} = -1/2$, $d_{11} = 0.2$. Only the neighborhood of the critical end point is shown.

These features can also be verified by analytic calculations. To this end, we will restrict ourselves to the vicinity of the critical end point and treat the symmetry-breaking term $\propto d_{11}$ in a perturbative fashion. In order to determine the λ-line, we take $b_2 < 0$ and $g \geq g_{\mathrm{e}}$, with $g_{\mathrm{e}} = g_{\mathrm{e}}(d_{11})$, the (as yet unknown) value of g at the critical end point. We write

$$\phi_\lambda(g) = \phi_\lambda^{(1)}(g)\,d_{11} + O(d_{11}^2), \tag{85}$$

$$\psi_\lambda(g) = \psi_+(g) + \psi_\lambda^{(2)}(g)\,d_{11}^2 + O(d_{11}^3), \tag{86}$$

and

$$a_{2\lambda}(g) = |d_{21}|\,\psi_+(g) + O(d_{11}^2)\,, \tag{87}$$

where $\psi_+(g)$ was defined in (44). The values of these quantities for $d_{11} = 0$ are known from our analysis of the symmetric critical end point in the previous subsection. That the term linear in d_{11} of $\psi_\lambda(g)$ vanishes follows from the fact that ϕ_λ and ϕ_λ are coupled *via* terms of order $d_{11}\,\phi_\lambda \sim \phi_\lambda^2 \sim d_{11}^2$. Upon substituting these expansions into the condition (80) and the expression (76) for $\tan\vartheta_\lambda$, we can solve for $\phi_\lambda^{(1)}(g)$, obtaining

$$\phi_\lambda^{(1)}(g) = \frac{-|d_{21}|}{2\,a_4\left[3\,b_4\,\psi_+^2(g) - b_2\right] - d_{21}^2} = \frac{-|d_{21}|\,\psi_+{}'(g)}{2\,\check{a}_4[\psi_+(g)]}\,, \tag{88}$$

where $\check{a}_4[\psi_+(g)]$ and $\psi_+{}'(g)$ are given by (51) and (47), respectively.

The above expansions can now be inserted into the equation of state (64) to determine h_λ. This gives

$$h_\lambda(g) = d_{11}\,\psi_+(g) + O(d_{11}^3). \tag{89}$$

Utilizing the result (67) for ψ_λ, one gets the second-order coefficient

$$\psi_\lambda^{(2)}(g) = -d_{11}^2\,\psi_+{}'(g)\,\phi_\lambda^{(1)}(g)\left[1 - \frac{|d_{21}|}{2}\,\phi_\lambda^{(1)}(g)\right]. \tag{90}$$

In order to be able to determine $g_{\rm e}$ from the coexistence condition

$$\mathcal{V}[\phi_\lambda,\psi_\lambda;a_{2\lambda}(g_{\rm e}),h_\lambda(g_{\rm e}),g_{\rm e}] = \mathcal{V}[\phi_\alpha,\psi_\alpha;a_{2\lambda}(g_{\rm e}),h_\lambda(g_{\rm e}),g_{\rm e}], \tag{91}$$

we must also know ψ_α and ϕ_α to the appropriate order in d_{11}. The corresponding series expansions are analogous to the those of ψ_λ and ϕ_λ given in (86) and (85). The zeroth-order term of ψ_α is $\psi_-(g) \equiv -\psi_+(-g)$ [*cf.* (38)]. Hence we have

$$[h - d_{11}\,\psi_\alpha]_\lambda = d_{11}\,[\psi_+(g) + \psi_+(-g)] + O(d_{11}^3) \tag{92}$$

and

$$[a_2 + d_{21}\,\psi_\alpha]_\lambda = |d_{21}|\,[\psi_+(g) + \psi_+(-g)] + O(d_{11}^2)\,. \tag{93}$$

To obtain ϕ_α on the λ-line, we insert these results into the expression (66) for η_0, which we expand in powers of its last argument, $[h - d_{11}\,\psi_\alpha]_\lambda$, using (36). This yields

$$\phi_\alpha|_\lambda = \frac{d_{11}}{|d_{21}|} + O(d_{11}^3), \tag{94}$$

which leads to

$$\psi_\alpha|_\lambda = -\psi_+(-g) - \frac{d_{11}^2}{2\,|d_{21}|}\,\psi_+{}'(-g) + O(d_{11}^3) \tag{95}$$

upon insertion into the expression (67) for η_-.

Using the above results, one can determine $g_{\rm e}(d_{11})$ to second order in d_{11} in a straightforward manner from the condition (91). The result is

$$g_{\rm e}(d_{11}) = \frac{d_{11}^2}{2\,|d_{21}|} + O(d_{11}^3). \tag{96}$$

As a check, let us set the interaction constants to the values $b_2 = -6$, $a_4 = b_4 = 1/6$, $d_{21} = -1/2$, $d_{11} = 0.2$ utilized in our numerical analysis (see Fig. 5). Our perturbative analytical results (96, 89), and (87) then predict the critical end point to be located at

$$\begin{aligned} g_{\rm e} &\simeq 0.04\,, \\ h_{\rm e} &= h_\lambda(g_{\rm e}) \simeq 1.2, \\ a_{2{\rm e}} &= a_{2\lambda}(g_{\rm e}) \simeq 3.0, \end{aligned} \tag{97}$$

and to have the slopes

$$\begin{aligned} h_\lambda{}'(g_{\rm e}) &\simeq d_{11}\,\psi_+{}'(g_{\rm e}) \simeq 0.017, \\ a_{2\lambda}{}'(g_{\rm e}) &\simeq |d_{21}|\,\psi_+{}'(g_{\rm e}) \simeq 0.04. \end{aligned} \tag{98}$$

These numbers are in excellent agreement with the numerical results shown in Figure 5.

Next, let us calculate the equilibrium densities $\phi_{\beta,\gamma}$ and $\psi_{\beta,\gamma}$ of the ordered phases β and γ in a perturbative manner. To this end, we consider a path in the space $\{(a_2,h,g)\}$ with $g = $ const. that is asymptotically parallel to the coexistence surface $\boldsymbol{\rho}$ and intersects the λ-line at a point $\mathcal{Q} = (a_{2\lambda}(g), h_\lambda(g), g)$ close or equal to the critical end point. Taking $\mathcal{Q}$ as expansion point in (77), we express the deviations $\delta\phi \equiv \phi - \phi_\lambda$ and $\delta\psi \equiv \psi - \psi_\lambda$ from the associated classical solution $(\phi_{\rm cl},\psi_{\rm cl}) = (\phi_\lambda,\psi_\lambda)$ in terms of the eigendensities φ_1 and φ_2 of $\mathcal{Q}$.

The shifts $\delta a_2 \equiv a_2 - a_{2\lambda}(g)$ and $\delta h = h - h_\lambda(g)$ induce the following changes of $\mathcal{V}(\phi,\psi)$: Nonvanishing terms

$$\frac{\delta a_2}{2}\cos(\vartheta_\lambda)\,\varphi_1^2 = \frac{\delta a_2}{2}\left[1 + O(d_{11}^2)\right]\varphi_1^2, \tag{99}$$

$$\frac{1}{2}\,\delta a_2\,\varphi_1\varphi_2\,\sin 2\vartheta_\lambda \sim d_{11}\,\delta a_2\,\varphi_1\varphi_2, \tag{100}$$

and[6]

$$\varphi_2\,[(\phi_\lambda\,\delta a_2 - \delta h)\sin\vartheta_\lambda] \sim d_{11}^2\,\varphi_2 \tag{101}$$

are generated; the coefficient $\lambda_2(\phi_\lambda,\psi_\lambda)$ of the $\frac{1}{2}\,{\varphi_2}^2$ term is changed by an amount $\delta a_2\,O(d_{11}^2)$. The term linear in φ_1 is negligible sufficiently close to $\mathcal{Q}$ since we required the path to be asymptotically parallel to the coexistence surface $\boldsymbol{\rho}$.

Minimizing with respect to φ_1 and φ_2 yields the equilibrium values

$$\varphi_{1\,\gamma}^{\,\beta} = \pm\sqrt{\frac{|\delta a_2|}{\check{a}_{4\lambda}}}\,\left[1 + o(\delta a_2)\right], \tag{102}$$

$$\varphi_{2\,\gamma}^{\,\beta} = \delta a_2\,O(d_{11}^2), \tag{103}$$

from which we get

$$\phi_{\,\gamma}^{\,\beta} - \phi_\lambda = \pm\sqrt{\frac{|\delta a_2|}{\check{a}_{4\lambda}}}\,\left[1 + o(\delta a_2)\right] \tag{104}$$

[6] Note that $\delta h \sim d_{11}$. Its zeroth-order term in d_{11} vanishes because the coexistence surface is given by $h = 0$ in this (symmetric) case.

and

$$\psi_{\substack{\beta\\ \gamma}} - \psi_\lambda \approx \psi_+{}'(g) \left[|d_{21}| \, \frac{|\delta a_2|}{\breve{a}_{4\lambda}} \mp d_{11} \sqrt{\frac{|\delta a_2|}{\breve{a}_{4\lambda}}} \right]. \quad (105)$$

Since $\delta a_2 \sim (-t)$, the result displays the expected $|t|^\beta$ singularity of (2), with the mean-field exponent $\beta = 1/2$.

In order to determine the wings of α-β and α-γ coexistence of the first-order surface $\boldsymbol{\sigma}$, we would have to substitute the classical equilibrium solutions $\phi_\wp$ and $\psi_\wp$, with $\wp = \alpha$, β, γ, into $\mathcal{V}(\phi, \psi)$ to obtain the corresponding grand potentials $\mathcal{A}_\wp(a_2, h, g)$ and then solve the coexistence conditions

$$\mathcal{A}_\alpha(a_2, h, g) = \mathcal{A}_l(a_2, h, g), \quad l = \beta, \gamma, \quad (106)$$

e.g., for g as a function of a_2 and h. On the triple line conditions (106) hold for both $l = \alpha$ and $l = \beta$.

Let us consider small deviations from the critical end point that are directed along the triple line. We parametrize these through $\delta a_2 \equiv a_2 - a_{2\mathrm{e}}$ and denote the value of the effective φ_1^4 interaction constant (84) at the critical end point as $\breve{a}_{4\mathrm{e}}$. Using the above results and neglecting terms of order d_{11}^2, it is not difficult to show that the triple-line value g_σ behaves as

$$g_\sigma \approx -\left[1 + O\big(d_{11}^2\big)\right] \frac{(\delta a_2)^2}{8\,\breve{a}_{4\mathrm{e}}\sqrt{|b_2|/b_4}} \quad (107)$$

as $\delta a_2 \sim t \to -0$. The second derivative of this expression with respect to t, taken at $t = +0$, gives us the expected jump singularity. (The corresponding value of $g_\sigma''(t)$ at $t = +0$ is zero.)

4 Beyond Landau theory

In the previous section we saw that Landau theory yields for both the symmetric and nonsymmetric versions of our model phase diagrams with the correct features. We also verified that the results of this approximation are consistent with the predicted singularities (1) and (2). We now wish to extend the analysis beyond Landau theory.

It will be helpful to make a number of remarks before we embark on details. Our strategy will be to relate the critical singularities on both the critical line *and* at the critical end point to those of the standard ϕ^4 theory. In other words, we will show that they can be described by a Hamiltonian of the form (6) of $\mathcal{H}_1[\phi]$. To understand how this works, it is useful to consider first the theories described by the Hamiltonians $\mathcal{H}_1[\phi]$ and $\mathcal{H}_2[\psi]$ in the absence of any coupling between ϕ and ψ, and then discuss what happens when $\mathcal{H}_{12}[\phi, \psi]$ is turned on.

4.1 The decoupled noncritical theory and redundant operators

Suppose that $B > 0$, $b_4 > 0$, $g = \pm 0$, and $b_2 < b_{2c}$, where b_{2c} is the critical value below which the symmetry $\psi \to -\psi$ is spontaneously broken. (At the level of Landau theory, $b_{2c} = 0$, of course.) Then $\mathcal{H}_2[\psi]$ describes a *massive* field theory whose statistical properties on length scales large compared to the corresponding correlation length ξ_ψ may be characterized by a Gaussian probability distribution with Hamiltonian

$$\frac{w_2}{2}\,\mathcal{H}_\mathrm{G}[\delta\psi] = \frac{w_2}{2}\int_\Omega \Big[\psi - \psi^{(\pm)}\Big]^2. \quad (108)$$

Here $\psi^{(\pm)}$ are the mean values of ψ in the pure phases selected by the choices $g = \pm 0$, respectively, while $\delta\psi$ denotes the fluctuating quantity inside the brackets on the right-hand side of (108). Hence the correlation function becomes

$$\langle \delta\psi(\boldsymbol{x})\, \delta\psi(\boldsymbol{x}')\rangle = w_2\, \delta(\boldsymbol{x} - \boldsymbol{x}') \quad (109)$$

for $|\boldsymbol{x} - \boldsymbol{x}'| \gg \xi_\psi$.

If we let $B \to 0$ in $\mathcal{H}_2[\psi]$, so that $\xi_\psi \to 0$, and ignore the cubic and quartic terms in (12), we obtain $w_2 = 2|b_2|$ and $\psi^{(\pm)} = \pm\sqrt{|b_2|/b_4}$. Inclusion of these terms (*e.g.*, by means of perturbation theory) does not modify this large-scale form of the theory's correlation functions, but produces different values of w_2 and $\psi^{(\pm)}$. In other words, the parameters of this Gaussian (fixed-point) Hamiltonian are changed, albeit its form remains the same. In RG theory such a change of coordinates of a fixed-point Hamiltonian in parameter space is known to be caused by *redundant* operators [43].

For the sake of clarity, let us briefly recall the concept of redundant operators. Consider a field theory with a Hamiltonian $\mathcal{H}[\varphi]$, where φ could be a single-component field, such as ϕ or ψ, or a multi-component field (φ^α), such as (ϕ, ψ). Suppose $\mathcal{H}^*[\varphi]$ is a fixed point under RG transformations. We consider operators of the form

$$\mathcal{O} = \int_\Omega \mathrm{d}^d x\, \mathcal{O}(\boldsymbol{x}), \quad \mathcal{O}(\boldsymbol{x}) = O[\varphi(\boldsymbol{x}), \nabla\varphi(\boldsymbol{x})], \quad (110)$$

i.e., $O(\boldsymbol{x})$ is a local operator depending on φ and its derivatives, but not explicitly on $\boldsymbol{x}$ (to ensure translational invariance.) Such an operator is called redundant if a local functional $\Upsilon(\boldsymbol{x}, [\varphi]) = \Upsilon[\varphi(\boldsymbol{x}), \nabla\varphi(\boldsymbol{x})]$ exists such that it can be written as

$$\mathcal{O}_\mathrm{red} = \mathfrak{G}_\mathrm{tra}[\Upsilon]\, \mathcal{H}^*[\varphi], \quad (111)$$

where $\mathfrak{G}_\mathrm{tra}[\Upsilon]$ is the generator of transformations of $\mathcal{H}$ induced by the change of variable

$$\varphi(\boldsymbol{x}) = \varphi'(\boldsymbol{x}) + \Upsilon(\boldsymbol{x}, [\varphi']). \quad (112)$$

That is,

$$\mathfrak{G}_\mathrm{tra}[\Upsilon]\, \mathcal{H}[\varphi] \equiv \int_\Omega \mathrm{d}^d x \left[\Upsilon(\boldsymbol{x}) \frac{\delta\mathcal{H}[\varphi]}{\delta\varphi(\boldsymbol{x})} - \frac{\delta\Upsilon(\boldsymbol{x})}{\delta\varphi(\boldsymbol{x})} \right], \quad (113)$$

where the second term in brackets results from the Jacobian of the transformation (112).

Now, consider the noncritical Gaussian Hamiltonian (13) or (108). This is a fixed point under RG transformations. Wegner (see Sect. III.G.2 of Ref. [43]) has shown

that *any operator $\mathcal{O}$ of the form (110) – i.e.*, the integral of any local operator – *at this Gaussian fixed point can be expressed as a sum of a redundant operator and a constant*:

$$\mathcal{O} = \mathcal{O}_{\rm red} + C_{\mathcal{O}}\,|\Omega|, \tag{114}$$

where the constant $C_{\mathcal{O}}$ may be zero for some operators (as it must for any operator that is odd in ψ). The result (114) can be proven in a constructive manner [47]. We content ourselves to showing how (114) reads for the cubic, quartic, and $(\nabla\psi)^2$ operators appearing in (12); one has

$$\int_\Omega \psi^3 = \frac{1}{2}\,\mathfrak{G}_{\rm tra}[\psi^2 + 2\,\delta(\mathbf{0})]\,\mathcal{H}_{\rm G}[\psi], \tag{115}$$

$$\int_\Omega \psi^4 = \frac{1}{2}\,\mathfrak{G}_{\rm tra}[\psi^3 + 3\,\psi\,\delta(\mathbf{0})]\,\mathcal{H}_{\rm G}[\psi] - 3|\Omega|\,[\delta(\mathbf{0})]^2, \tag{116}$$

and

$$\int_\Omega (\nabla\psi)^2 = \frac{1}{2}\,\mathfrak{G}_{\rm tra}[-\nabla^2\psi]\,\mathcal{H}_{\rm G}[\psi] + |\Omega| \int_{\boldsymbol{q}} q^2. \tag{117}$$

In a theory regularized by a cutoff Λ the momentum integration $\int_{\boldsymbol{q}} = \int \mathrm{d}^d q/(2\pi)^d$ is restricted by $|\boldsymbol{q}| \le \Lambda$; thus $\delta(\mathbf{0}) = \int_{\boldsymbol{q}} 1$ is not infinite but equal to $K_d\,\Lambda^d$, with $K_d = 2^{1-d}\pi^{-d/2}/\Gamma(d/2)$.

It is useful to recall the physical significance of the result (114): The massive field theory described by $\mathcal{H}_2[\psi]$ does not exhibit critical singularities; the associated bulk free energy density is an analytic function of the thermodynamic fields. Thus no scaling operators other than the trivial one $|\Omega|$ appear; the associated scaling field is the previously mentioned special one with RG eigenexponent d.

4.2 The decoupled critical theory

We next turn to the field theory described by the Hamiltonian $\mathcal{H}_1[\phi]$. For given positive values of A and a_4, this has a critical point at $(a_2, h) = (a_{2c}, 0)$, where $a_{2c} = 0$ in the Landau approximation. The asymptotic behavior at this critical point can be analyzed by means of well-known RG methods [48–50]. In order to establish our notation, it is necessary that we briefly recapitulate some of its ingredients.

Let us introduce the corresponding bulk free energy (per volume and $k_{\rm B}T$)

$$f_{1,\rm b}(a_2, a_4, h) = -\lim_{\Omega\uparrow\mathbb{R}^d} \left\{ \frac{1}{|\Omega|} \ln \int \mathcal{D}\phi\, \mathrm{e}^{-\mathcal{H}_1[\phi]} \right\} \tag{118}$$

as well as the generating functionals $\mathcal{Z}_1[J, I]$ and $\mathcal{G}_1[J, I]$ of correlation functions and cumulants, respectively, *via*

$$\mathcal{Z}_1[J, I] = \mathrm{e}^{\mathcal{G}_1[J,I]} = \left\langle \mathrm{e}^{(J,\phi)+\frac{1}{2}(I,\phi^2)} \right\rangle_{\mathcal{H}_1}, \tag{119}$$

where the subscript $\mathcal{H}_1$ serves to indicate that the average

$$\langle\,.\,\rangle_{\mathcal{H}_1} \equiv \frac{\int \mathcal{D}\phi\, \mathrm{e}^{-\mathcal{H}_1[\phi]}}{\int \mathcal{D}\phi\, \mathrm{e}^{-\mathcal{H}_1[\phi]}} \tag{120}$$

refers to the decoupled system with Hamiltonian $\mathcal{H}_1[\phi]$ (rather than to the full one with Hamiltonian $\mathcal{H}[\phi, \psi]$), and

$$(I, \phi^2) \equiv \int_\Omega \mathrm{d}^d x\, I(\boldsymbol{x})\, \phi^2(\boldsymbol{x}) \tag{121}$$

is a convenient shorthand.

To absorb the ultraviolet (uv) divergences of the theory in $d = 4 - \epsilon \le 4$ dimensions, we use reparametrizations of the form

$$\phi = [Z_\phi(u)]^{1/2}\ \phi_{\rm ren}, \tag{122}$$

$$a_2 = \kappa^2\, Z_\tau(u)\, \tau + a_{2,c}, \tag{123}$$

$$a_4 = \kappa^\epsilon\, Z_u(u)\, u, \tag{124}$$

$$h = \kappa^{(d+2)/2}\, [Z_\phi(u)]^{-1/2}\, h_{\rm ren}. \tag{125}$$

Here κ is an arbitrary momentum scale. The renormalization factors are understood to be fixed my means of a τ ('mass') independent renormalization scheme; for concreteness, we shall assume that dimensional regularization is employed and that they are determined by minimal subtraction of poles in ϵ. In a cutoff-regularized theory, the shift $a_{2,c}$ of the critical point from its zero-loop value 0 diverges as Λ^2 as $\Lambda \to \infty$.

In addition to the reparametrizations (122–125), additive counterterms are required. The bulk free energy $f_{1,\rm b}$ and its first and second derivatives with respect to a_2 have primitive divergences $\sim \Lambda^4$, $\sim \Lambda^2$ and $\sim \ln\Lambda$ at $d = 4$, respectively. To cancel these, we make subtractions at the normalization point (NP) $a_2 = a_2^{\rm NP}$, $h = 0$, with

$$a_2^{\rm NP} = a_{2,c} + \kappa^2\, Z_\tau\, \tau^{\rm NP}, \quad \tau^{\rm NP} = 1. \tag{126}$$

Accordingly we introduce the renormalized bulk free energy

$$\begin{aligned} f_{1,\rm b}^{\rm ren}(\tau, u, h_{\rm ren}) = {} & f_{1,\rm b}(a_2, a_4, h) - f_{1,\rm b}^{\rm NP}(a_4) \\ & - \left(a_2 - a_2^{\rm NP}\right) \varepsilon^{\rm NP}(a_4) \\ & + \frac{1}{2}\left(a_2 - a_2^{\rm NP}\right)^2 C^{\rm NP}(a_4), \end{aligned} \tag{127}$$

where the renormalization functions $\varepsilon^{\rm NP}$ and $C^{\rm NP}$ are fixed through the normalization conditions

$$f_{1,\rm b}^{\rm ren}(1, u, 0) = 0, \tag{128}$$

$$\frac{\partial f_{1,\rm b}^{\rm ren}}{\partial \tau}(1, u, 0) = 0, \tag{129}$$

and

$$\frac{\partial^2 f_{1,\rm b}^{\rm ren}}{\partial \tau^2}(1, u, 0) = 0. \tag{130}$$

For the generating functional of renormalized cumulants we have (*cf.* Sect. 12.1.1 of Ref. [48])

$$\mathcal{G}_1^{\rm ren}[J,I] = \mathcal{G}_1\Big[Z_\phi^{-1/2}J, Z_\tau\, I\Big] - \int_\Omega \Big\{\varepsilon^{\rm NP} Z_\tau\, I - \frac{1}{2}\, C^{\rm NP}\, \big[Z_\tau\, I - \big(a_2 - a_2^{\rm NP}\big)\,\big]^2\Big\}. \quad (131)$$

Thus the renormalized cumulants

$$G_{1,\rm ren}^{(N,M)} = \left.\frac{\delta^{N+M}\mathcal{G}_1^{\rm ren}[J,I]}{\delta J(\boldsymbol{x}_1)\ldots\delta J(\boldsymbol{x}_N)\,\delta I(\boldsymbol{X}_1)\ldots\delta I(\boldsymbol{X}_M)}\right|_{\substack{J=0\\I=0}} \quad (132)$$

are related to their analogously defined bare counterparts $G_1^{(N,M)}$ *via*

$$G_{1,\rm ren}^{(N,M)} = Z_\phi^{-N/2}\, Z_\tau^M \Big\{G_1^{(N,M)} - \delta_{M,1}^{N,0}\,\big[\varepsilon^{\rm NP} - C^{\rm NP}\,\kappa^2\, Z_\tau\,(\tau-1)\big] + \delta_{M,2}^{N,0}\, C^{\rm NP}\,\delta(\boldsymbol{X}_{12})\Big\}, \quad (133)$$

where $\boldsymbol{X}_{12} = \boldsymbol{X}_1 - \boldsymbol{X}_2$.

Upon varying κ, we can derive RG equations. Let us introduce the beta function

$$\beta_u(u) = \kappa\partial_\kappa|_0\, u, \quad (134)$$

the exponent functions

$$\eta_\phi(u) = \kappa\partial_\kappa|_0\, \ln Z_\phi, \quad (135)$$

$$\eta_\tau(u) = \kappa\partial_\kappa|_0\, \ln Z_\tau, \quad (136)$$

and the differential operator

$$\mathcal{D}_\kappa \equiv \kappa\partial_\kappa + \beta_u\partial_u - (2+\eta_\tau)\tau\partial_\tau - \frac{d+2-\eta_\phi}{2}\, h_{\rm ren}\partial_{h_{\rm ren}}, \quad (137)$$

where $\partial_\kappa|_0$ means a derivative at fixed values of the bare parameters a_2, a_4, and h. Then the RG equations can be written as

$$\mathcal{D}_\kappa\, f_{b,1}^{\rm ren} = -\frac{2+\eta_\tau}{2}\,(\tau-1)^2\,\big(\partial_\tau^3 f_{1,\rm b}^{\rm ren}\big)^{\rm NP} \quad (138)$$

and

$$\left[\mathcal{D}_\kappa + \frac{N}{2}\,\eta_\phi - M\,\eta_\tau\right] G_{1,\rm ren}^{(N,M)} = -\frac{2+\eta_\tau}{\kappa^{2M}}\,\big(\partial_\tau^3 f_{1,\rm b}^{\rm ren}\big)^{\rm NP}\,\Big[\delta_{M,1}^{N,0}\,(\tau-1) - \delta_{M,2}^{N,0}\Big]. \quad (139)$$

The RG equations (138) and (139) can be exploited in a standard fashion to derive the familiar scaling forms of the (singular part of the) free energy and of the cumulants $G_{1,\rm ren}^{(N,M)}$. Details can be found, for instance, in references [48–50] or [51] and will not be repeated here. In the cases of the free energy $f_{1,\rm b}^{\rm ren}$, the energy density $\varepsilon^{\rm ren} = G_{1,\rm ren}^{(0,1)}$, and $G_{1,\rm ren}^{(0,2)}$ (specific heat) the RG equations are inhomogeneous. Explicit solutions to such equations in terms of RG trajectory integrals are given in reference [52] (and elsewhere). Specifically for the renormalized free energy $f_{1,\rm b}^{\rm ren}$, the solution reads

$$f_{1,\rm b}^{\rm ren}(\tau, h_{\rm ren}, u, \kappa) = (\kappa\ell)^d\, f_{1,\rm b}^{\rm ren}[\bar\tau(\ell), \bar h(\ell), \bar u(\ell), 1] + \int_1^\ell \frac{{\rm d}\ell'}{\ell'}\,\bar I(\ell'). \quad (140)$$

with

$$\bar I(\ell) = -\frac{2+\eta_\tau[\bar u(\ell)]}{2}\,[\bar\tau(\ell)-1]^2\,\big(\partial_\tau^3 f_{1,b}^{\rm ren}\big)^{\rm NP}(\bar u, \kappa\ell) = -\frac{2+\eta_\tau[\bar u(\ell)]}{2}\,\frac{\kappa^d\,\ell^{3/\nu}\,[\bar\tau(\ell)-1]^2}{[E_\tau(\bar u(\ell), u)]^3}\,\big(\partial_\tau^3 f_{1,\rm b}^{\rm ren}\big)^{\rm NP}(u,1), \quad (141)$$

where $\bar u(\ell)$, $\bar\tau(\ell)$, and $\bar h(\ell)$ are standard running variables (*cf.* Eqs. (3.79a), (3.79b), and (3.79d) of Ref. [51]). Utilizing the notational conventions of this reference, we have

$$\bar\tau(\ell) = \ell^{-1/\nu}\, E_\tau[\bar u(\ell), u]\,\tau \underset{\ell\to0}{\approx} \ell^{-1/\nu}\, E_\tau^*(u)\,\tau \quad (142)$$

and

$$\bar h(\ell) = \ell^{-\Delta/\nu}\, E_h[\bar u(\ell), u]\, h \underset{\ell\to0}{\approx} \ell^{-\Delta/\nu}\, E_h^*(u)\, h_{\rm ren}. \quad (143)$$

Here

$$E_\tau[\bar u, u] = \exp\left\{\int_u^{\bar u(\ell)} {\rm d}x\, \frac{\eta_\tau^* - \eta_\tau(x)}{\beta_u(x)}\right\} \quad (144)$$

and

$$E_h[\bar u, u] = \exp\left\{\int_u^{\bar u(\ell)} {\rm d}x\, \frac{\eta_\phi(x) - \eta}{\beta_u(x)}\right\}. \quad (145)$$

An asterisk is used to mark values at the infrared-stable fixed point u^* of the beta function β_u. Further, $E_{\tau,h}^*(u)$ means $E_{\tau,h}(u^*, u)$, and the exponents are given by $\nu = (2+\eta_\tau^*)^{-1}$ and $\Delta/\nu = (d+2-\eta_\phi^*)/2$, respectively.

The consequences of these equations for the free energy $f_{1,\rm b}^{\rm ren}$ can be cast in the usual form: It is a sum of a regular and a singular part,

$$f_{1,\rm b}^{\rm ren} = f_{1,\rm b}^{\rm reg} + f_{1,\rm b}^{\rm sing}. \quad (146)$$

The latter, a solution of the homogeneous RG equation of $f_{1,\rm b}^{\rm ren}$, near criticality takes the scaling form

$$f_{1,\rm b}^{\rm sing}(\tau, h_{\rm ren}, u) \approx |\hat\tau|^{2-\alpha}\, Y_\pm(\hat h\,|\hat\tau|^{-\Delta}). \quad (147)$$

Here $\hat\tau \approx E_\tau^*(u)\,\tau$ and $\hat h \approx E_h^*(u)\, h_{\rm ren}$ are the two relevant scaling fields. The scaling function $Y_\pm(y)$ is universal (and hence independent of u); its two branches $\pm$ satisfy matching conditions as $y \to \pm\infty$ (see, *e.g.*, Ref. [11]).

4.3 The coupled theory

We are now ready to discuss the coupled theory, with $\mathcal{H}_{12} \neq 0$. We begin with the symmetric case, setting $h = d_{11} = 0$ and $A = 1$. To simplify the subsequent analysis, we also set the interactions constants e_{21} and f_{21} to zero, but will comment on their effects later (see the paragraph following Eq. (163)).

4.3.1 Symmetric case

As reference densities about which we expand we take the classical solutions $\phi_{\rm cl} = 0$ and $\psi_{\rm cl}$ at a point $(a_2, h, g) = (a_{2\lambda}^{\rm cl}(g_{\rm cl}), 0, g_{\rm ref})$ with $g_{\rm ref} \geq g_e$ on the Landau-theory λ-line. Writing

$$\psi = \psi_{\rm cl} + \check{\psi}, \tag{148}$$

we have

$$\mathcal{H}[\phi,\psi] = \mathcal{H}_2[\psi_{\rm cl}] + \check{\mathcal{H}}[\phi,\check{\psi}] + \mathcal{H}'[\phi,\check{\psi}] \tag{149}$$

with

$$\check{\mathcal{H}}[\phi,\check{\psi}] = \int_\Omega \Big[\frac{1}{2}\,(\nabla\phi)^2 + \frac{\check{a}_2}{2}\,\phi^2 + \frac{a_4}{4}\,\phi^4 + \frac{\check{b}_2}{2}\,\check{\psi}^2 + \frac{d_{21}}{2}\,\phi^2\,\check{\psi}\Big] \tag{150}$$

and

$$\mathcal{H}'[\phi,\check{\psi};\psi_{\rm cl}] = \int_\Omega \Big[\frac{B}{2}\,\big(\nabla\check{\psi}\big)^2 + \frac{\check{b}_3(\psi_{\rm cl})}{3}\,\check{\psi}^3 + \frac{b_4}{4}\,\check{\psi}^4\Big], \tag{151}$$

where

$$\check{a}_2 = a_2 + d_{21}\,\psi_{\rm cl}, \tag{152}$$

$$\check{b}_2 = b_2 + 3b_4\,\psi_{\rm cl}^2, \tag{153}$$

$$\check{b}_3 = 3b_4\,\psi_{\rm cl}. \tag{154}$$

Suppose first that $\mathcal{H}'$ is neglected. Since $\check{\mathcal{H}}$ is quadratic in $\check{\psi}$, having the same form as the Hamiltonian of the stochastic dynamic models C, D, and E [44], the field $\check{\psi}$ can then be integrated out exactly to obtain an effective ϕ^4 model. Let us define quite generally, both for $\mathcal{H}' = 0$ as well as for $\mathcal{H}' \neq 0$, an effective Hamiltonian through

$$\mathrm{e}^{-\mathcal{H}_{\rm eff}[\phi]} \equiv \int \mathcal{D}\check{\psi}\,\mathrm{e}^{-\mathcal{H}_2[\psi_{\rm cl}] - \check{\mathcal{H}}[\phi,\check{\psi}] - \mathcal{H}'[\phi,\check{\psi}]}. \tag{155}$$

For $\mathcal{H}' = 0$ we have

$$\mathcal{H}_{\rm eff}[\phi] = \frac{1}{2}\,\ln\frac{\check{b}_2}{2\pi} + \mathcal{H}_1[\phi;\check{a}_2,a_4^{\rm eff}] \tag{156}$$

where $\mathcal{H}_1[\phi;\check{a}_2,a_4^{\rm eff}]$ is the $h = 0$ variant of the Hamiltonian (6), with a_2 and a_4 replaced by expression (152) for $\check{a}_2$ and

$$a_4^{\rm eff} = a_4 - \frac{d_{21}^2}{2\,\check{b}_2}, \tag{157}$$

respectively. Thus, if $\mathcal{H}'$ can be set to zero, the critical behavior of the Hamiltonian (149) reduces indeed to that of a ϕ^4 model. This result is, of course, not new: it has been used in the construction and analyses of the dynamic models C, D, and E for a long time (*cf.* also Ref. [30]).

Next, consider what happens when $\mathcal{H}'$ is included. A straightforward calculation shows that the cubic and quartic terms of $\mathcal{H}'$ can be rewritten as

$$\int_\Omega \check{\psi}^3 = \mathfrak{G}_{\rm tra}[\Upsilon_3]\,\check{\mathcal{H}}[\phi,\check{\psi}] - \int_\Omega \Big[\frac{d_{21}^3}{8\,\check{b}_2^3}\,\phi^6 + \frac{3\,d_{21}\,\delta(\mathbf{0})}{2\,\check{b}_2^2}\,\phi^2\Big] \tag{158}$$

and

$$\int_\Omega \check{\psi}^4 = \mathfrak{G}_{\rm tra}[\Upsilon_4]\,\check{\mathcal{H}}[\phi,\check{\psi}] + \int_\Omega \Big[\frac{d_{21}^4}{16\,\check{b}_2^4}\,\phi^8 + \frac{3\,d_{21}^2\,\delta(\mathbf{0})}{2\,\check{b}_2^3}\,\phi^4 + \frac{3\,[\delta(\mathbf{0})]^2}{\check{b}_2^2}\Big] \tag{159}$$

with

$$\Upsilon_3 = \frac{\check{\psi}^2}{\check{b}_2} - \frac{d_{21}\,\phi^2}{2\,\check{b}_2^2}\,\check{\psi} + \frac{d_{21}^2\,\phi^4 + 8\,\check{b}_2\,\delta(\mathbf{0})}{4\,\check{b}_2^3} \tag{160}$$

and

$$\Upsilon_4 = \frac{\check{\psi}^3}{\check{b}_2} - \frac{d_{21}\phi^2}{2\,\check{b}_2^2}\,\check{\psi}^2 + \frac{d_{21}^2\phi^4 + 12\,\check{b}_2\,\delta(\mathbf{0})}{4\,\check{b}_2^3}\,\check{\psi} - \frac{d_{21}\,\phi^2}{8\,\check{b}_2^4}\big[20\,\check{b}_2\,\delta(\mathbf{0}) + d_{21}^2\,\phi^4\big]. \tag{161}$$

The meaning of these results is the following. To first order in the coupling constants $\check{b}_3$ and b_4, the terms $\propto \int_\Omega \check{\psi}^3$ and $\propto \int_\Omega \check{\psi}^4$ can be transformed away at the expense of (i) additional irrelevant interactions ($\propto \phi^n$, with $n = 6, 8$), (ii) contributions $\propto |\Omega|$, and (iii) a change of the coefficients of the ϕ^2 and ϕ^4 terms.

The irrelevant interactions may be dropped. (iii) can be absorbed through a redefinition of the temperature-like scaling field and the irrelevant scaling field $\sim u - u^*$, which hence become dependent on $\check{b}_3$ and b_4 (as well as on d_{21} and $\check{b}_2$). (ii) means contributions $\propto \check{b}_3$ and $\propto b_4$ to the constant part of the Hamiltonian, which we write as $\mu_0\,|\Omega|$, where μ_0 is Wegner's *special* scaling field (*cf.* Sect. III.G.2 of Ref. [43]). Since $\check{b}_2$ depends *via* $\psi_{\rm cl}$ on the nonordering field g, these contributions to μ_0 have *g-dependent parts*.

We are now ready to understand the origin and nature of the discontinuity eigenperturbation indicated in Figure 2. Let $\mu_0^{(\lambda)}(g) \equiv \mu_0[a_{2\lambda}(g), g]$ be the value of μ_0 at a point $(a_{2\lambda}(g), h{=}0, g)$ on the λ-line[7], and $\mu_0^{(\rm e)} \equiv \mu_0^{(\lambda)}(g_{\rm e})$, the corresponding critical-end-point value. Consider a variation $g_{\rm e} \to g_{\rm e} + \delta g$, $a_{2\rm e} \to a_{2\rm e} + \delta a_2$ along the

[7] We suppress the dependence of μ_0 and $a_{2\lambda}$ on the other variables, b_2, b_4, etc. Instead of the variables $a_2, \ldots$ one could, of course, also use $\check{a}_2, \ldots$. Yet we prefer to express μ_0 in terms of the former.

λ-line. This induces a change

$$\delta\mu_0^{(\lambda)} = \mu_0^{(\lambda)}(g) - \mu_0^{(\mathrm{e})} \tag{162}$$

of the special scaling field μ_0, with $\delta\mu_0^{(\lambda)} \sim T_{\mathrm{c}}(g) - T_{\mathrm{e}}$ for small δg. The shift of the Hamiltonian $\delta\mu_0^{(\lambda)}\,|\Omega|$ is an eigenperturbation with eigenexponent $y = d$. Obviously this is the one we were looking for and whose eigendirection is shown in Figure 2.

We still have to consider the $(\nabla\check{\psi})^2$ term of $\mathcal{H}'$. Power counting tells us that it is irrelevant. One also verifies that it can be rewritten as

$$\int_\Omega (\nabla\check{\psi})^2 = \mathfrak{G}_{\mathrm{tra}}[-\check{b}_2^{-1}\Delta\check{\psi}]\,\check{\mathcal{H}}[\phi,\check{\psi}] + \check{b}_2^{-1}\int_\Omega\left[\frac{d_{21}}{2}\,\phi^2\,\Delta\check{\psi} + \int_{\boldsymbol{q}} q^2\right]. \tag{163}$$

The last term in the second line contributes again to the constant part $\mu_0\,|\Omega|$ of the Hamiltonian. The first one, proportional to $\int_\Omega \phi^2\,\Delta\psi$, is irrelevant according to power counting, which conforms with our expectation that the interaction (163) is irrelevant (apart from contributions to the constant part of the Hamiltonian) and can be dropped. Finally, power counting also indicates that the terms involving e_{21} and f_{21} are irrelevant, so that they may be omitted as well.

Having identified the sought discontinuity eigenperturbation (162) and knowing that it does not contribute to the critical singularities on the λ-line or at the end point, we can now focus directly on these, dropping the $\check{\psi}^3$ and $\check{\psi}^4$ interactions as well as the $(\nabla\check{\psi})^2$ term (163). From equations (155) and (156) we know already that the resulting truncated Hamiltonian $\check{\mathcal{H}}$ reduces to an effective ϕ^4 Hamiltonian upon integrating out $\check{\psi}$. Moreover, the Hamiltonian $\check{\mathcal{H}}$ and its renormalization are well known from studies of the stochastic dynamic models C, D, and E (see, *e.g.*, Refs. [53,54], or Sect. 35.4 of [48]). Adding a source term $-\int_\Omega \check{I}\,\check{\psi}$ to $\check{\mathcal{H}}$, one can compute the functional integral $\int\mathcal{D}\check{\psi}\,\exp\{-\check{\mathcal{H}}[\phi,\check{\psi}] + \int_\Omega \check{I}\check{\psi}\}$ to relate the cumulants $\langle\prod_{j=1}^N \phi(\boldsymbol{x}_j)\,\prod_{i=1}^M \psi(\boldsymbol{X}_i)\rangle_{\check{\mathcal{H}}}^{\mathrm{cum}}$ pertaining to $\check{\mathcal{H}}$ to cumulants of a standard ϕ^4 theory described by the Hamiltonian (156). One has

$$\langle\check{\psi}(\boldsymbol{X})\rangle_{\check{\mathcal{H}}} = -\frac{d_{21}}{2\check{b}_2}\,\langle\phi^2(\boldsymbol{X})\rangle_{\mathcal{H}_{\mathrm{eff}}} \tag{164}$$

and

$$\langle\check{\psi}(\boldsymbol{X}_1)\,\check{\psi}(\boldsymbol{X}_2)\rangle_{\check{\mathcal{H}}}^{\mathrm{cum}} = \frac{\delta(\boldsymbol{x}_{12})}{\check{b}_2} + \frac{d_{21}^2}{4\,\check{b}_2^2}\,\langle\phi^2(\boldsymbol{X}_1)\,\phi^2(\boldsymbol{X}_2)\rangle_{\mathcal{H}_{\mathrm{eff}}}^{\mathrm{cum}}. \tag{165}$$

All other correlation functions of the fields $\check{\psi}$ and ϕ are identical to their analogs of the effective ϕ^4 theory one obtains through the replacement

$$\check{\psi}(\boldsymbol{X}) \to -\frac{d_{21}}{2\check{b}_2}\,\phi^2(\boldsymbol{X}). \tag{166}$$

Thus the critical behavior of the above cumulants $\langle\prod_{j=1}^N \phi(\boldsymbol{x}_j)\,\prod_{i=1}^M \psi(\boldsymbol{X}_i)\rangle_{\check{\mathcal{H}}}^{\mathrm{cum}}$ may be inferred directly from the known one of the corresponding cumulants of the ϕ^4 theory. Alternatively, one could derive RG equations for the former, using the reparametrizations $a_4^{\mathrm{eff}} = \kappa^\epsilon\,Z_u(u)\,u$, $\phi = Z_\phi^{1/2}(u)\,\phi_{\mathrm{ren}}$, $\check{\psi} = \check{b}_2^{-1/2}\,Z_\psi^{1/2}(u,\gamma)\,\check{\psi}_{\mathrm{ren}}$, $a_2^{\mathrm{eff}} = \kappa^2\,Z_\tau(u)\,\tau + a_{2,c}^{\mathrm{eff}}$, $\check{a}_2 = \kappa^2\,Z_\psi(u,\gamma)\,Z_\tau(u)\,\check{\tau} + \check{a}_{2,c}$, and $d_{21} = \check{b}_2^{1/2}\,\kappa^{\epsilon/2}\,Z_\psi^{1/2}(u,\gamma)\,Z_\tau(u)\,\gamma$. Here Z_u, Z_ϕ, and Z_τ are the renormalization factors introduced in equations (122–125), while Z_ψ is of the form $Z_\psi(u,\gamma) = 1/[1-\gamma^2\,f(u)]$, where $f(u)$ is known to be given by the Laurent part of the additive counterterm $\propto I^2$ in equation (131) [53,54].

From equation (131) we see that the leading singularity of $\langle\check{\psi}\rangle$ (and hence of $\langle\psi\rangle$) on a path with $\tau \sim T - T_{\mathrm{c}}(g)$ agrees with that of the energy density $\langle\phi^2\rangle$. Since on the liquid branch of the liquid-gas coexistence boundary the scaling field τ varies asymptotically linearly in $t \sim T - T_{\mathrm{e}}$ as the critical end point is approached, the leading singularity of the density $\varrho_{\mathrm{tot}} = \langle\psi\rangle$ is indeed of the form $V_\pm^0\,|t|^{1-\alpha}$, where V_+^0/V_-^0 is the usual universal specific-heat amplitude ratio.

4.3.2 Nonsymmetric case

Considering points (a_2, h, g) on the $\beta\gamma$ (disordered) side of the coexistence surface $\boldsymbol{\rho}$, we expand about the classical solutions $\phi_{\beta\gamma}^{\mathrm{cl}}$ and $\psi_{\beta\gamma}^{\mathrm{cl}}$. Since we ultimately wish to approach the λ-line or critical end point, we may restrict ourselves to points in their immediate vicinity. Introducing the shifted densities $\check{\psi}$ and $\check{\psi}$ *via*

$$\phi = \phi_{\mathrm{cl}} + \check{\phi}\,, \quad \psi = \psi_{\mathrm{cl}} + \check{\psi}, \tag{167}$$

we express the Hamiltonian defined through equations (3) and (6–8) in terms of these. The resulting quadratic ("Gaussian") part can be written as

$$\mathcal{H}_{\mathrm{G}} = \frac{1}{2}\int_\Omega (\check{\phi}\,,\ \check{\psi})\left[\boldsymbol{\mathcal{V}}_{\mathrm{cl}}^{(2)} - \boldsymbol{\eta}_{\mathrm{cl}}\,\Delta\right]\begin{pmatrix}\check{\phi}\\ \check{\psi}\end{pmatrix} \tag{168}$$

with

$$\boldsymbol{\eta}_{\mathrm{cl}} \equiv \begin{pmatrix} A + f_{21}\,\psi_{\mathrm{cl}} & e_{11} + e_{21}\,\phi_{\mathrm{cl}} \\ e_{11} + e_{21}\,\phi_{\mathrm{cl}} & B \end{pmatrix} \tag{169}$$

and $\boldsymbol{\mathcal{V}}_{\mathrm{cl}}^{(2)} \equiv \boldsymbol{\mathcal{V}}^{(2)}(\phi_{\mathrm{cl}}, \psi_{\mathrm{cl}})$, where $\boldsymbol{\mathcal{V}}^{(2)}$ is the matrix introduced in equation (72).

The matrix $\boldsymbol{\eta}_{\mathrm{cl}}$ must be positive definite. [Otherwise, the classical homogeneous states $(\phi_{\mathrm{cl}}, \psi_{\mathrm{cl}})$ are not guaranteed to be stable.] It plays the role of a metric. Hence we can diagonalize $\mathcal{H}_{\mathrm{G}}$ by a similarity transformation

$$\begin{pmatrix}\check{\phi}\\ \check{\psi}\end{pmatrix} = \boldsymbol{U}\cdot\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix}, \tag{170}$$

satisfying the diagonalization condition (74) together with the orthonormality relation

$$\boldsymbol{U}^{\mathrm{T}}\cdot\boldsymbol{\eta}_{\mathrm{cl}}\cdot\boldsymbol{U} = \mathbf{1}, \tag{171}$$

to obtain

$$\mathcal{H}_{\rm G} = \frac{1}{2}\int_\Omega \big[(\nabla\varphi_1)^2 + \lambda_1\,\varphi_1^2 + (\nabla\varphi_2)^2 + \lambda_2\,\varphi_2^2\big]. \quad (172)$$

By analogy with equations (149–151), we split the resulting total Hamiltonian (3) as

$$\mathcal{H}[\phi,\psi] = \mathcal{H}[\phi_{\rm cl},\psi_{\rm cl}] + \check{\mathcal{H}}[\varphi_1,\varphi_2] + \mathcal{H}'[\varphi_1,\varphi_2] \quad (173)$$

with

$$\check{\mathcal{H}}[\varphi_1,\varphi_2] = \int_\Omega \bigg[\frac{1}{2}\,(\nabla\varphi_1)^2 + \frac{\lambda_1}{2}\,\varphi_1^2 + \frac{v_{4,0}}{4}\,\varphi_1^4 + \frac{\lambda_2}{2}\,\varphi_2^2 + \frac{v_{2,1}}{2}\,\varphi_1^2\,\varphi_2\bigg] \quad (174)$$

and

$$\mathcal{H}'[\varphi_1,\varphi_2] = \int_\Omega \bigg[\frac{1}{2}\,(\nabla\varphi_2)^2 + \sum_{j=3}^{4}\frac{v_{0,j}}{j}\,\varphi_2^j + v_{1,2}\,\varphi_1\,\varphi_2^2 + v_{3,1}\,\varphi_1^3\,\varphi_2 + v_{1,3}\,\varphi_1\,\varphi_2^3 + v_{2,2}\,\varphi_1^2\,\varphi_2^2 + \frac{e_{21}}{2}\,\check{\phi}^2\Delta\check{\psi} + \frac{f_{21}}{2}\,\big(\nabla\check{\phi}\big)^2\psi\bigg]. \quad (175)$$

We have dropped a contribution $v_{3,0}\,\varphi^3$ to the integrand of $\mathcal{H}'$; its coupling constant $v_{3,0}$ vanishes at the Landau-theory location of the λ-line by condition (79), and we know already that it can be transformed away by means of a shift $\varphi_1 \to \varphi_1 + \Phi_1$; *i.e.*, aside from a change of the interaction constants of the Hamiltonian $\check{\mathcal{H}}$ and its constant part, it corresponds to a sum of redundant and irrelevant operators.

The Hamiltonian $\check{\mathcal{H}}$ has the familiar model-C form (150). The contributions in the first line of equation (175) are the analogs of the Hamiltonian (151); from our considerations in Section 4.3.1 we know their effect: Apart from contributing to the special scaling field (and shifting the λ-line and critical end point), they involve redundant and irrelevant operators, and hence may be dropped when analyzing the asymptotic critical behavior. The same is true of the remaining terms of (151). The easiest way to arrive at this conclusion is *via* power counting, utilizing the canonical scale dependences $\varphi_1 \sim \kappa^{1-\epsilon/2}$ and $\varphi_2 \sim \kappa^{2-\epsilon/2}$. Moreover, the contributions involving the interaction constants $v_{1,2}\,,\ldots\,,v_{2,2}$ could be analyzed along the same lines as the $\check{\psi}^3$ and $\check{\psi}^4$ nonlinearities in the previous subsection by choosing appropriate functionals $\Upsilon[\varphi_2]$ to eliminate them *via* a change of variable $\varphi_2 \to \varphi_2 + \Upsilon[\varphi_2]$. The contributions proportional to e_{21} and f_{21} correspond to a variety of derivative terms $\varphi_1^2\triangle\varphi_1$, $\varphi_1^2\triangle\varphi_2$, $\ldots$, $(\nabla\varphi_2)^2\varphi_2$, all of which are irrelevant according to power counting.

Upon ignoring $\mathcal{H}'$ altogether, we get back to the Hamiltonian $\check{\mathcal{H}}[\varphi_1,\varphi_2]$, which is equivalent to the one in equation (150). The implications for the asymptotic critical behavior that occurs when the λ-line or the critical end point are approached is obvious: φ_1, the order parameter, and the secondary density φ_2 behave asymptotically as their respective analogs ϕ and ψ in the symmetric case.

The density ψ has components along both φ_1 and φ_2. Consequently its average $\varrho_{\rm tot} = \langle\psi\rangle$ has singularities of the form $U_\pm^0\,|t|^\beta$ (with $U_+^0 \equiv 0$) and $V_\pm^0\,|t|^{1-\alpha}$ in the limit $t \equiv (T - T_{\rm e})/T_{\rm e} \to \pm 0$. This holds, in particular, for approaches along the coexistence boundary $g_\sigma(t)$. Thus the leading singularity of the liquid density $\varrho_{\rm tot}$ is $\sim |t|^\beta$ if the critical end point is approached along the triple line, and $\sim |t|^{1-\alpha}$ if it is approached along the $\beta\gamma$-α section of the liquid-gas coexistence line. These findings are in conformity with equation (2).

4.3.3 The singularity of the first-order line $g_\sigma(t)$

A crucial assumption on which the phenomenological derivation [5] of the $|t|^{2-\alpha}$ singularity of the first-order line $g_\sigma(t)$ is based is the asymptotic behavior of the grand potentials $\mathcal{A}_\wp$ of the phases $\wp = \beta$, γ, and $\beta\gamma$ at the critical end point. This is hypothesized to be of the same form as at a conventional critical point; *i.e.*, it can be decomposed by analogy with equation (146) into a regular background contribution and a nonanalytic part, $\mathcal{A}_\wp^{\rm sing}$, which has the asymptotic scaling form (147).

Keeping in mind our identification (162) of the discontinuity eigenperturbation, one realizes that our above field-theoretic considerations are in full accordance with these assumptions, corroborating them. Utilizing them one can proceed [39] just as in the derivation [5] based on the phenomenological scaling theory to determine the coexistence singularity of the first-order boundary $g_\sigma(t)$ from the coexistence conditions (56). Since $\hat{\tau} \sim t$ for small deviations from the critical end point directed along $g_\sigma(t)$, this line inherits the $|t|^{2-\alpha}$ singularity of the grand potentials $\mathcal{A}_{\beta\gamma}$ and $\mathcal{A}_{\beta,\gamma}$. Thus equation (1) follows.

5 Summary and conclusion

To put things in perspective, it will be helpful to recapitulate the main steps of our analysis and summarize its principal results.

(i) In order to study the critical behavior at symmetric and nonsymmetric critical end points as well as the associated coexistence singularities, phenomenological continuum models with a Hamiltonian depending on two fluctuating densities ϕ and ψ were introduced. These models may be viewed as continuum variants of the BEG model [33]. They generalize similar ones previously considered in the literature (*cf.* Ref. [13]), to which they reduce when some interaction constants vanish. We justified them *via* phenomenological arguments, but were also able to derive them directly from the BEG model, utilizing a generalized Kac-Hubbard-Stratonovich transformation to map the latter exactly on a lattice field theory and a subsequent continuum approximation.

(ii) We then employed Landau theory to analyze the models for the cases in which the Hamiltonian obeys or

breaks the symmetry $\phi \to -\phi$. Provided the interactions constants were chosen in the appropriate ranges, phase diagrams with either a symmetric or nonsymmetric critical end point could be obtained (*cf.* Figs. 3–5). Furthermore, we corroborated that the $|t|^{2-\alpha}$ singularity (1) of the first-order line $g_\sigma(t)$ and the $|t|^{1-\alpha}$ and $|t|^\beta$ coexistence singularities (2) of $\langle\psi\rangle$ take on the expected Landau-theory forms, namely, discontinuities in the second derivative of $g_\sigma(t)$ and in the first derivative of $\langle\psi\rangle$, or a singularity $\sim |t|^{1/2}$, respectively.

(iii) Building on these results, we then studied the critical behavior on the λ-line and at the critical end point. One important observation was the following. In order to obtain phase diagrams with a critical end point (in Landau theory and beyond), it was *essential to include nonlinearities* such as a ψ^4 term *that are irrelevant according to power counting*. The presence of this term guarantees that a stable α (gas) phase exists, even in the absence of coupling to the (primary) order-parameter density ϕ. However, once it has been verified that the phase diagram has the correct topology (with a critical line λ, critical end point, and first-order boundary $g_\sigma(t)$), one can focus on the more specific problem of the asymptotic critical behavior that occurs when either a point on the λ-line or else the critical end point itself is approached along a given thermodynamic path. Then approximations that are tailored for this particular purpose become viable.

Upon expanding about the classical equilibrium values of the densities ϕ and ψ, and expressing the Hamiltonian in terms of the deviations $\check{\phi}$ and $\check{\psi}$ from these, the Hamiltonian was found to involve also nonlinearities that are *irrelevant* according to power counting, such as the $\check{\psi}^3$ and $\check{\psi}^4$ terms in the symmetric case. We were able to show, within the context of perturbation theory, what their effects are: Aside from (a) inducing *a change of the usual two scaling fields* (the temperature-like scaling field τ and the magnetic-field like scaling field), they (b) correspond to *irrelevant operators* (giving rise to corrections to scaling) and (c) contribute to the *constant part of the fixed-point Hamiltonian*, *i.e.*, to Wegner's [43] *special* scaling field μ_0.

(iv) These findings enabled us to verify the existence of a discontinuity eigenexponent d at the fixed point representing the critical end point, and to understand its origin: The eigenperturbation with which it is associated corresponds to the change $\delta\mu_0$ of the special scaling field μ_0 that occurs when one moves away from the critical end point such that the theory remains critical.

(v) In conjunction with the findings mentioned at the end of (iii), (iv) shows that the critical behavior on the λ-line is the same as at the critical end point, inasmuch as the values of the critical exponents and other universal quantities are concerned.

We emphasize that our conclusions mentioned in (iv) and (v) are in conformity with the position-space RG results of references [22,25] and the RG picture that has emerged from them (*cf.* Fig. 2). Our results show how this RG picture translates into field theory; they verify the existence of the discontinuity eigenexponent, clarify its origin, and reveal how its presence can be reconciled with the anticipated equality of the critical exponents associated with the critical line and the critical end point, respectively.

(vi) Once we had established the results (iv) and (v), we could derive the coexistence singularities (1) and (2) in a fairly straightforward fashion. The $|t|^{1-\alpha}$ singularities in equation (1) are due to the coupling of the secondary density, ψ, to the energy density. In the case of a *symmetric* critical end point, this is the leading temperature singularity of $\langle\psi\rangle$ on the liquid branch of the liquid-gas coexistence curve. In the case of a *nonsymmetric* critical end point, the densities ϕ and ψ mix. Thus the order parameter becomes a linear combination, φ_1, of both, so that ψ couples directly to φ_1. This implies that the leading coexistence singularity of $\langle\psi\rangle$ on the three-phase-coexistence side of the transition becomes $\sim |t|^\beta$. The $|\tau|^{2-\alpha}$ of the first-order boundary $g_\sigma(t)$ follows in a way known from its original phenomenological derivation [5] from the usual free-energy singularity of the $\beta\gamma$, β, and γ phases at the critical end point.

(vii) A challenging issue raised by Fisher and Barbosa in their critical assessment [3] of the theory of critical end points, is the potential occurrence of essential singularities at first-order boundaries like $\boldsymbol{\sigma}$. Since our approach relied on perturbative RG arguments, essential singularities are beyond its scope.

The following should also be clear: We cannot, of course, rule out that for special models the critical behavior at the critical end point might differ from that on the critical line. However, this should not happen in the generic cases we were concerned with here.

(viii) The present work, which was focused exclusively on *bulk* properties, provides a basis for investigating the problem of critical adsorption at a noncritical α-$\beta\gamma$ interface. This issue will be taken up in a separate publication.

(ix) We close with a comment on possible implications of the recent work by Fisher *et al.* [55,56] that appeared after completion of the present investigation. Upon reanalyzing two-phase heat-capacity data of the one-component fluid propane (C_3H_8), these authors concluded that both contributions to the specific heat

$$C_V^{\rm tot} = VT(\partial^2 p/\partial T^2)_V - NT(\partial^2\mu/\partial T^2)_V \,, \qquad (176)$$

the pressure derivative $\mathrm{d}^2p/\mathrm{d}T^2 \equiv p''_{\rm vp}$ *and* the chemical potential derivative $\mathrm{d}^2\mu/\mathrm{d}T^2 \equiv \mu''_{\rm vp}$ diverge as $|t|^{-\alpha}$ when $t \equiv (T - T_{\rm c})/T_{\rm c} \to -0$ on the vapor-pressure curve. This behavior, which Yang and Yang [57] originally suggested to be the most likely one for real gases, differs from that of simple lattice gas models, for which $\mu_{\rm vp}$ is found to be analytic through $T_{\rm c}$ so that $\mu''_{\rm vp}(T_{\rm c}-)$ must remain finite. Building on Rehr and Mermin's earlier work [58], Fisher and Orkoulas [55] concluded that the standard scaling theory for fluid criticality must be revised inasmuch as the pressure difference $p - p_{\rm c}$ should, in general, also mix into the scaling fields, in addition to the chemical potential and temperature differences $\mu - \mu_{\rm c}$ and t, respectively. As a remarkable consequence of this 'pressure mixing' they found that the arithmetic mean $(\rho_{\rm l} + \rho_{\rm g})/2$ of the gas and

liquid densities $\rho_{\rm l,g}$ at coexistence should have a temperature singularity $\sim |t|^{2\beta}$ as $t \to -0$. Such a singularity would dominate over the usual energy-density singularity $\sim |t|^{1-\alpha}$ that is usually given in textbooks [4] as the leading one of this quantity.

If this pressure mixing must indeed be taken into account in the analysis of critical behavior of simple fluids, one anticipates it to play a role also in the case of critical behavior at nonsymmetric critical end points. Clearly, the leading singularity $\sim |t|^{\beta}$ of the coexistence density (2) must prevail, but one expects pressure mixing to produce a subleading one of the form $|t|^{2\beta}$, which would be stronger than the subleading singularity $\sim |t|^{1-\alpha}$ included in equation (2).

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Appendix: Mapping of the BEG model onto a field theory

We start from the Hamiltonian (14) of the BEG model. To set up the Hubbard-Stratonovich transformation, we introduce the row vectors

$$\boldsymbol{\sigma} = \left(\dots, S_{\boldsymbol{i}}, \dots, S_{\boldsymbol{j}}^2, \dots\right), \tag{177}$$

$$\boldsymbol{F} = (\dots, H_{\boldsymbol{i}} = H, \dots, D_{\boldsymbol{j}} = D, \dots), \tag{178}$$

the transposed column vector $\boldsymbol{\sigma}^{\rm T}$, and the matrix

$$\boldsymbol{M} = \begin{pmatrix} \boldsymbol{J} + M_0\,\boldsymbol{1} & \boldsymbol{L} \\ \boldsymbol{L} & \boldsymbol{K} + M_0\,\boldsymbol{1} \end{pmatrix}. \tag{179}$$

Here $\boldsymbol{J} = (J_{\boldsymbol{ij}})$, $\boldsymbol{K} = (K_{\boldsymbol{ij}})$, and $\boldsymbol{L} = (L_{\boldsymbol{ij}})$ are the matrices of interaction constants, *i.e.*, $J_{\boldsymbol{ij}}$ takes the value J or vanishes, depending on whether $\boldsymbol{i}$ and $\boldsymbol{j}$ are nearest neighbors or not, and likewise for $\boldsymbol{L}$ and $\boldsymbol{K}$. The parameter M_0 has been chosen such that the matrix $\boldsymbol{M}$ is positive definite (*cf.* [46] and [59]), so that the inverse of $\boldsymbol{M}$ exists.

With these definitions the Hamiltonian (14) can we written as

$$\mathcal{H}_{\rm BEG} = -\frac{1}{2}\,\boldsymbol{\sigma}\cdot(\boldsymbol{M} - M_0)\cdot\boldsymbol{\sigma}^{\rm T} - \boldsymbol{F}\cdot\boldsymbol{\sigma}^{\rm T}. \tag{180}$$

Proceeding in a standard fashion by making a Gaussian transformation, we can perform the trace over the spin variables in the partition function (18). This gives

$$\mathcal{Z}_{\rm BEG} = {\rm e}^{-f_0}\left(\prod_{\boldsymbol{i}}\int_{-\infty}^{\infty}{\rm d}\phi_{\boldsymbol{i}}\int_{-\infty}^{\infty}{\rm d}\psi_{\boldsymbol{i}}\right){\rm e}^{-\mathcal{H}_{\rm lft}[\phi,\psi]} \tag{181}$$

with

$$f_0 = \frac{1}{2}\,{\rm Tr}\ln\left[2\pi\,(\boldsymbol{M} - M_0)\right] \tag{182}$$

and

$$\mathcal{H}_{\rm lft} = \frac{1}{2}\sum_{\boldsymbol{i}\neq\boldsymbol{j}}\left[\phi_{\boldsymbol{i}}\,\mathcal{P}_{\boldsymbol{ij}}\,\phi_{\boldsymbol{j}} + \psi_{\boldsymbol{i}}\,\mathcal{Q}_{\boldsymbol{ij}}\,\psi_{\boldsymbol{j}} + \mathcal{R}_{\boldsymbol{ij}}\,(\phi_{\boldsymbol{i}}\,\psi_{\boldsymbol{j}} + \psi_{\boldsymbol{i}}\,\phi_{\boldsymbol{j}})\right] + \sum_{\boldsymbol{i}} w(\phi_{\boldsymbol{i}},\psi_{\boldsymbol{i}}), \tag{183}$$

where

$$w(\phi_{\boldsymbol{i}},\psi_{\boldsymbol{i}}) = \frac{1}{2}\left(\mathcal{P}_{\boldsymbol{ii}}\,\phi_{\boldsymbol{i}}^2 + 2\,\mathcal{R}_{\boldsymbol{ii}}\,\phi_{\boldsymbol{i}}\,\psi_{\boldsymbol{i}} + \mathcal{Q}_{\boldsymbol{ii}}\,\psi_{\boldsymbol{i}}^2\right) - \ln\left[1 + 2\,{\rm e}^{\psi_{\boldsymbol{i}} + D - M_0}\cosh(\phi_{\boldsymbol{i}} + H)\right], \tag{184}$$

while $\mathcal{P}_{\boldsymbol{ij}}$, $\mathcal{Q}_{\boldsymbol{ij}}$, and $\mathcal{R}_{\boldsymbol{ij}}$ are the elements of the matrices

$$\boldsymbol{\mathcal{P}} = \left[\boldsymbol{J} + M_0 - \boldsymbol{L}\,(\boldsymbol{K} + M_0)^{-1}\,\boldsymbol{L}\right]^{-1} = \frac{1}{M_0}\left[\boldsymbol{1} - \frac{\boldsymbol{J}}{M_0} + \frac{\boldsymbol{J}^2 + \boldsymbol{L}^2}{M_0^2} + \dots\right], \tag{185}$$

$$\boldsymbol{\mathcal{Q}} = \left[\boldsymbol{K} + M_0 - \boldsymbol{L}\,(\boldsymbol{J} + M_0)^{-1}\,\boldsymbol{L}\right]^{-1} = \frac{1}{M_0}\left[\boldsymbol{1} - \frac{\boldsymbol{K}}{M_0} + \frac{\boldsymbol{K}^2 + \boldsymbol{L}^2}{M_0^2} + \dots\right], \tag{186}$$

and

$$\boldsymbol{\mathcal{R}} = -\left[\boldsymbol{J} + M_0\right]^{-1}\,\boldsymbol{L}\left[\boldsymbol{K} + M_0 - \boldsymbol{L}\,(\boldsymbol{J} + M_0)^{-1}\,\boldsymbol{L}\right]^{-1} = \frac{1}{M_0}\left[-\frac{\boldsymbol{L}}{M_0} + \frac{\boldsymbol{L}\boldsymbol{J} + \boldsymbol{K}\boldsymbol{L}}{M_0^2} + \dots\right], \tag{187}$$

respectively. Thus the BEG model (14) is exactly equivalent to a lattice-field theory with Hamiltonian (183).

Just as in the simpler Ising case [46,59], the bonds of this Hamiltonian (*i.e.*, the off-diagonal elements $-\mathcal{P}_{\boldsymbol{ij}}$, $-\mathcal{Q}_{\boldsymbol{ij}}$, and $-\mathcal{R}_{\boldsymbol{ij}}$) extend beyond nearest neighbors (NN). From the expansions given in the second line of (185–187) one sees that the NN couplings are given by $\boldsymbol{J}/M_0^2$, $\boldsymbol{K}/M_0^2$, and $\boldsymbol{L}/M_0^2$, respectively, up to corrections that are smaller by a factor M_0^{-1}. Likewise, next-nearest-neighbor couplings are down by this factor, compared to the NN bonds.

In our interpretation of the BEG model as a model for binary fluids, interchanging A and B particles corresponds to the transformation $S_{\boldsymbol{i}} \to -S_{\boldsymbol{i}}$ for all sites $\boldsymbol{i}$. Consequently, $\mathcal{H}_{\rm BEG}$ is AB-symmetric if $H = L = 0$. In this case, $\mathcal{H}_{\rm lft}$ evidently is *even* in ϕ, as it must.

So far our reformulation of the BEG model has been exact. We now make a continuum approximation. Introducing smoothly interpolating fields $(\phi_\upsilon(\boldsymbol{x})) \equiv (\phi(\boldsymbol{x}), \psi(\boldsymbol{x}))$, we write $\phi_{\boldsymbol{i}}^\upsilon = \phi_\upsilon(a\boldsymbol{i})$, where a is the lattice constant, and use the expansion

$$\phi_{\boldsymbol{i}}^\upsilon - \phi_{\boldsymbol{j}}^\upsilon = \boldsymbol{r}_{\boldsymbol{ij}}\cdot\nabla\phi_\upsilon\left[a\,(\boldsymbol{i} + \boldsymbol{j})/2\right] + \dots \tag{188}$$

for small $\boldsymbol{r_{ij}} = a\,(\boldsymbol{i}-\boldsymbol{j})$. (To simplify our analysis, we take the sites $\boldsymbol{i}$ to be those of a simple d-dimensional cubic lattice with periodic boundary conditions.)

In this manner we obtain from $\mathcal{H}_{\rm lft}$ the Hamiltonian

$$\mathcal{H}[\phi,\psi] = \int_\Omega \mathrm{d}^d x \Big\{ \frac{1}{2}\,\phi_\upsilon \left(\overleftarrow{\nabla}\, A_{\upsilon\upsilon'} \nabla + T_{\upsilon\upsilon'} \right) \phi_{\upsilon'} \\ a^{-d}\, w(\phi,\psi) \Big\} \tag{189}$$

with

$$(A_{\upsilon\upsilon'}) = \frac{-1}{2d\,a^d} \sum_{\boldsymbol{j}\neq\boldsymbol{0}} \begin{pmatrix} \mathcal{P}_{\boldsymbol{0j}} & \mathcal{R}_{\boldsymbol{0j}} \\ \mathcal{R}_{\boldsymbol{0j}} & \mathcal{Q}_{\boldsymbol{0j}} \end{pmatrix} \boldsymbol{r}_{\boldsymbol{0j}}^2 \tag{190}$$

and

$$(T_{\upsilon\upsilon'}) = a^{-d} \sum_{\boldsymbol{j}\neq\boldsymbol{0}} \begin{pmatrix} \mathcal{P}_{\boldsymbol{0j}} & \mathcal{R}_{\boldsymbol{0j}} \\ \mathcal{R}_{\boldsymbol{0j}} & \mathcal{Q}_{\boldsymbol{0j}} \end{pmatrix}. \tag{191}$$

Here $\overleftarrow{\nabla}$ acts to the left, while ∇ acts as usual to the right. Derivatives of higher than second order have been dropped.

For the BEG model (14) with NN interactions and positive values of the NN bonds J, K, and L, the matrix $(A_{\upsilon\upsilon'})$ is positive definite provided $J+K>2L$. To see this note that

$$(A_{\upsilon\upsilon'}) = \frac{1}{a^d\,d}\,\frac{\mathrm{d}}{\mathrm{d}q^2}\,\tilde{\boldsymbol{M}}(\boldsymbol{q})\big|_{\boldsymbol{q}=0} \tag{192}$$

where

$$\tilde{\boldsymbol{M}}(\boldsymbol{q}) \equiv \left(\sum_{\boldsymbol{j}\neq\boldsymbol{0}} M_{\boldsymbol{0j}}^{\upsilon\upsilon'}\, \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\boldsymbol{0}\jmath}} \right) \tag{193}$$

is the Fourier transform of $\boldsymbol{M}$. But

$$\frac{\mathrm{d}}{\mathrm{d}q^2}\,\tilde{\boldsymbol{M}}(\boldsymbol{q}) = -\tilde{\boldsymbol{M}}(\boldsymbol{q}) \cdot \frac{\mathrm{d}\tilde{\boldsymbol{M}}(\boldsymbol{q})^{-1}}{\mathrm{d}q^2} \cdot \tilde{\boldsymbol{M}}(\boldsymbol{q}) \tag{194}$$

and

$$-\frac{\mathrm{d}}{\mathrm{d}q^2}\tilde{\boldsymbol{M}}(\boldsymbol{q})^{-1}\big|_{\boldsymbol{q}=\boldsymbol{0}} = a^2 \begin{pmatrix} J & L \\ L & K \end{pmatrix}. \tag{195}$$

The latter is positive definite because of our assumption $J+K>2L$. In conjunction with (194) it follows that $\mathrm{d}\tilde{\boldsymbol{M}}(\boldsymbol{q})/\mathrm{d}q^2$ and hence $(A_{\upsilon\upsilon'})$ are also positive definite. Thus $(A_{\upsilon\upsilon'})$ provides a metric, and the quadratic form

$$\left(T_{\upsilon\upsilon'} + a^{-d}\,\frac{\partial^2 w(\phi,\psi)}{\partial\phi_\upsilon\,\partial\phi_{\upsilon'}}\Big|_{\phi=\psi=0} \right) \phi_\upsilon(\boldsymbol{x})\,\phi_{\upsilon'}(\boldsymbol{x}) \tag{196}$$

can be diagonalized by a similarity transformation

$$\varphi_\upsilon(\boldsymbol{x}) = U_{\upsilon\upsilon'}\,\phi_{\upsilon'}(\boldsymbol{x}), \tag{197}$$

where $(U_{\upsilon\upsilon'}) \equiv \boldsymbol{U}$ is orthogonal with respect to the metric $(A_{\upsilon\upsilon'})$:

$$\boldsymbol{U}^{\mathrm{T}} \cdot (A_{\upsilon\upsilon'}) \cdot \boldsymbol{U} = \boldsymbol{1}\,. \tag{198}$$

For vanishing L, $(A_{\upsilon\upsilon'})$ is diagonal, but for $L\neq 0$ it is not and the quadratic part of the Hamiltonian (189) must be diagonalized by such a linear transformation. Thus even at this Gaussian level of the theory, the fields ϕ and ψ 'mix', *i.e.*, the order parameter becomes a linear combination of ϕ and ψ, a feature that is expected quite generally in the nonsymmetric case $L\neq 0$, $H\neq 0$.

To compute the interaction constants $A_{\upsilon\upsilon'}$, we expand in L, keeping only contributions up to first order in L. This yields

$$A = \frac{1}{2d\,a^d\,M_0} \sum_{\boldsymbol{j}\neq\boldsymbol{0}} \left[\boldsymbol{J}\,(M_0+\boldsymbol{J})^{-1} \right]_{0\mathrm{j}} \boldsymbol{r}_{0\mathrm{j}}^2 + O\big(L^2\big), \tag{199}$$

$$B = \frac{1}{2d\,a^d\,M_0} \sum_{\boldsymbol{j}\neq\boldsymbol{0}} \left[\boldsymbol{K}\,(M_0+\boldsymbol{K})^{-1} \right]_{0\mathrm{j}} \boldsymbol{r}_{0\mathrm{j}}^2 + O\big(L^2\big), \tag{200}$$

and

$$e_{11} = -\frac{1+O\big(L^2\big)}{2d\,a^d\,M_0} \sum_{\boldsymbol{j}\neq\boldsymbol{0}} \big[(M_0+\boldsymbol{J})^{-1}\boldsymbol{L}\,(M_0+\boldsymbol{K})^{-1} \\ + (M_0+\boldsymbol{K})^{-1}\boldsymbol{L}\,(M_0+\boldsymbol{J})^{-1} \big]_{0\mathrm{j}}\, \boldsymbol{r}_{0\mathrm{j}}^2. \tag{201}$$

Finally, we expand the function $w(\phi,\psi)$ in equation (189) into powers of ϕ and ψ, eliminate the resulting ϕ^3 and ψ^3 terms through the shifts (10) and (5), and drop terms of sufficiently high order. The resulting continuum Hamiltonian then takes the form specified by equations (3) and (6–8), except that the coupling constants e_{21} and f_{21} vanish in the used approximation. However, such interaction terms will be generated when one coarse-grains to a larger scale by integrating out the corresponding short wavelength degrees of freedom.

References

1. For background, see [2–4]. A typical phase diagram with such a critical end point is shown in Figure 1 of [3], for example.
2. R.B. Griffiths, J. Chem. Phys. **60**, 195 (1973).
3. M.E. Fisher, M.C. Barbosa, Phys. Rev. B **43**, 11177 (1991).
4. P.M. Chaikin, T.C. Lubensky, *Principles of condensed matter theory* (Cambridge University Press, Cambridge (GB), 1995).
5. M.E. Fisher, in *Proceedings of the Gibbs Symposium, Yale University, 1989*, edited by D. Caldi, G.D. Mostow (American Mathematical Society, Rhode Island, 1990), pp. 39–72.
6. P.H. van Konynenburg, R.L. Scott, Philos. Trans. R. Soc. London, Ser. A **298**, 495 (1979).
7. B. Widom, J. Chem. Phys. **67**, 872 (1977).
8. T.A.L. Ziman, D.J. Amit, G. Grinstein, C. Jayaprakash, Phys. Rev. B **25**, 319 (1982).
9. B. Widom, Chem. Soc. Rev. **14**, 121 (1985).

10. M.E. Fisher, P.J. Upton, Phys. Rev. Lett. **65**, 2402 (1990).
11. M.E. Fisher, P.J. Upton, Phys. Rev. Lett. **65**, 3405 (1990).
12. B.M. Law, Ber. Bunsenges. Phys. Chem. **98**, 472 (1994).
13. N.B. Wilding, Phys. Rev. Lett. **78**, 1488 (1997).
14. N.B. Wilding, Phys. Rev. E **55**, 6624 (1997).
15. N.B. Wilding, F. Schmid, P. Nielaba, Phys. Rev. E **58**, 2201 (1998).
16. M.C. Barbosa, M.E. Fisher, Phys. Rev. B **43**, 10 635 (1991).
17. R.L. Scott, P.H. van Konynenburg, Discuss. Faraday Soc. **49**, 87 (1970).
18. T. Getta, S. Dietrich, Phys. Rev. E **47**, 1856 (1993).
19. D. Roux, C. Coulon, M.E. Cates, J. Phys. Chem. **96**, 4174 (1992).
20. S. Dietrich, A. Latz, Phys. Rev. B **40**, 9204 (1989).
21. M.C. Barbosa, Physica A **177**, 153 (1991).
22. A.N. Berker, M. Wortis, Phys. Rev. B **14**, 4946 (1976).
23. M.E. Fisher, Physica A **172**, 77 (1991).
24. V.L. Ginzburg, A.A. Sobyanin, Sov. Phys. Usp. **31**, 289 (1988), [Usp. Fiz. Nauk. **154**, 545–563 (1988)].
25. M. Kaufman, R.B. Griffiths, J.M. Yeomans, M.E. Fisher, Phys. Rev. B **23**, 3448 (1981).
26. T.H. Magerlein, T.M. Sanders Jr., Phys. Rev. Lett. **36**, 258 (1978).
27. F. Ramos-Gómez, B. Widom, Physica A **104**, 595 (1980).
28. A.A. Sobyanin, Sov. Phys. JETP **34**, 229 (1972), [Zh. Eksp. Teor. Fiz. **61**, 433–438 (1971)].
29. P. Tavan, B. Widom, Phys. Rev. B **27**, 180 (1983).
30. A.Z. Patashinskiĭ, V.L. Pokrovskiĭ, S.B. Khokhlachev, Sov. Phys. JETP **36**, 807 (1973), [Zh. Eksp. Teor. Fiz. **63**, 1521–1524 (1972)].
31. B. Groh, S. Dietrich, in *New Approaches to Old and New Problems in Liquid State Theory: Inhomogeneities and Phase Separation in Simple, Complex and Quantum Fluids*, edited by C. Caccamo, J.P. Hansen, G. Stell (Kluwer, Dordrecht, 1998), p. 147.
32. B. Nienhuis, M. Nauenberg, Phys. Rev. Lett. **35**, 477 (1975).
33. M. Blume, V.J. Emery, R.B. Griffiths, Phys. Rev. A **4**, 1071 (1971).
34. M.E. Fisher, P.-G. de Gennes, C.R. Acad. Sci. Paris Série B **287**, 207 (1978).
35. A.J. Liu, M.E. Fisher, Phys. Rev. A **40**, 7202 (1989).
36. H.W. Diehl, Ber. Bunsenges. Phys. Chem. **98**, 466 (1994).
37. G. Flöter, S. Dietrich, Z. Phys. B **97**, 213 (1995).
38. H.W. Diehl, M. Smock, Physica A **281**, 268 (2000), `cond-mat/9908311`.
39. M. Smock, *Kritische Adsorption in zweikomponentigen Flüssigkeitsmischungen in der Umgebung des kritischen Endpunkts*, *Dissertation Universität-Gesamthochschule Essen* (Shaker Verlag, Aachen, 1999).
40. M. Smock, H.W. Diehl (unpublished).
41. S. Dietrich, in *Phase Transitions and Critical Phenomena*, edited by C. Domb, J.L. Lebowitz (Academic, London, 1988), Vol. 12, pp. 1–218.
42. In a RG analysis of the asymptotic behavior at the critical line or end point, it would be most convenient to set $A = 1$ and to transform b_2 to the value ± 1 (depending on whether the original b_2 is positive or negative). The main reason we do not do this here is that we wish to retain b_2 as a variable for use in our analysis of the bulk phase diagram.
43. F.J. Wegner, in *Phase Transitions and Critical Phenomena*, edited by C. Domb, M.S. Green (Academic, London, 1976), Vol. 6, Chap. 2, pp. 7–124.
44. B.I. Halperin, P.C. Hohenberg, S.-K. Ma, Phys. Rev. Lett. **29**, 1548 (1972).
45. J. Sivardière, J. Lajzerowicz, Phys. Rev. A **11**, 2090 (1975).
46. M.E. Fisher, in *Critical Phenomena*, Vol. 186 of *Lecture Notes in Physics*, edited by F.J.W. Hahne (Springer-Verlag, Berlin, 1983), pp. 117–121.
47. See Sect. III.G.2 of [43]. Wegner's elegant proof utilizes some general sophisticated RG formalism. For the proof of statement (114) this is not necessary; one can proceed in a more elementary fashion, by considering the action of $\mathfrak{G}_{\rm tra}[\Upsilon]$ on $\mathcal{H}_{\rm G}[\psi]$ for arbitrary monomials Υ in ψ and by writing $\mathcal{O}$ as a sum of integrals $\int_\Omega$ of such monomials.
48. J. Zinn-Justin, *Quantum Field Theory and Critical Phenomena*, *International series of monographs on physics*, 3rd edn. (Clarendon Press, Oxford, 1996).
49. E. Brézin, J.C.L. Guillou, J. Zinn-Justin, in *Phase Transitions and Critical Phenomena*, edited by C. Domb, M.S. Green (Academic, London, 1976), Vol. 6, Chap. 3, pp. 125–247.
50. D.J. Amit, *Field theory, the renormalization group, and critical phenomena*, 2nd edn. (World Scientific, Singapore, 1989).
51. H.W. Diehl, in *Phase Transitions and Critical Phenomena*, edited by C. Domb, J.L. Lebowitz (Academic, London, 1986), Vol. 10, pp. 75–267.
52. H.W. Diehl, S. Dietrich, Z. Phys. B **43**, 315 (1981).
53. E. Brézin, C. de Dominicis, Phys. Rev. B **12**, 4954 (1975).
54. E. Eisenriegler, B. Schaub, Z. Phys. B **39**, 65 (1980).
55. M.E. Fisher, G. Orkoulas, Phys. Rev. Lett. **85**, 696 (2000).
56. G. Orkoulas, M.E. Fisher, C. Üstün, J. Chem. Phys. **113**, 7530 (2000).
57. C.N. Yang, C.P. Yang, Phys. Rev. Lett. **13**, 303 (1964).
58. J.J. Rehr, N.D. Mermin, Phys. Rev. A **8**, 472 (1973).
59. H.W. Diehl, A. Ciach, Phys. Rev. B **44**, 6642 (1991).