

Asymmetric fluid criticality. I. Scaling with pressure mixing

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(Received 11 December 2002; published 30 June 2003)

The thermodynamic behavior of a fluid near a vapor-liquid and, hence, asymmetric critical point is discussed within a general “complete” scaling theory incorporating pressure mixing in the nonlinear scaling fields as well as corrections to scaling. This theory allows for a Yang-Yang anomaly in which $\mu''_{\sigma}(T)$, the second temperature derivative of the chemical potential along the phase boundary, diverges like the specific heat when $T \rightarrow T_c$; it also generates a leading singular term, $|t|^{2\beta}$, in the coexistence curve diameter, where $t \equiv (T - T_c)/T_c$. The behavior of various special loci, such as the critical isochore, the critical isotherm, the k -inflection loci, on which $\chi^{(k)} \equiv \chi(\rho, T)/\rho^k$ (with $\chi = \rho^2 k_B T K_T$) and $C_V^{(k)} \equiv C_V(\rho, T)/\rho^k$ are maximal at fixed T , is carefully elucidated. These results are useful for analyzing simulations and experiments, since particular, nonuniversal values of k specify loci that approach the critical density most rapidly and reflect the pressure-mixing coefficient. Concrete illustrations are presented for the hard-core square-well fluid and for the restricted primitive model electrolyte. For comparison, a discussion of the classical (or Landau) theory is presented briefly and various interesting loci are determined explicitly and illustrated quantitatively for a van der Waals fluid.

DOI: 10.1103/PhysRevE.67.061506

PACS number(s): 64.70.Fx, 05.70.Jk, 64.60.Fr

I. INTRODUCTION AND OVERVIEW

In 1964 Yang and Yang [1] derived the thermodynamic relation

$$C_V^{\text{tot}}(T, V) = VT \left(\frac{\partial^2 p}{\partial T^2} \right) - NT \left(\frac{\partial^2 \mu}{\partial T^2} \right), \quad (1.1)$$

for a fluid at pressure p , chemical potential μ , and temperature T , where V is the volume and N the number of particles, while C_V^{tot} is the constant-volume specific heat or, better, heat capacity. This has since been called the Yang-Yang relation [2]. When it is applied to the two-phase region beneath the critical temperature T_c , one has $p = p_{\sigma}(T)$ and $\mu = \mu_{\sigma}(T)$ (where σ denotes the phase boundary on which liquid and vapor may coexist), and the partial derivatives become total derivatives. Since the observations of Voronel' and co-workers in 1962–63 [3] it has been well established that the heat capacity $C_V^{\text{tot}}(T)$ diverges weakly along the phase boundary when the critical point is approached. The divergence of C_V^{tot} then implies that one, the other, or both of the second derivatives $p''_{\sigma}(T)$ and $\mu''_{\sigma}(T)$ must diverge when $T \rightarrow T_c$ along the phase boundary. The lattice gas model and its standard variants predict that μ''_{σ} remains finite at T_c while p''_{σ} diverges like the specific heat [4]. However, Yang and Yang suggested that in real fluids *both* should diverge [1]: clearly this is a basic issue for the description and understanding of criticality in fluids.

Recently, Fisher and co-workers [2] carefully analyzed experimental two-phase heat-capacity data for propane (C_3H_8) and CO_2 and showed that the evidence rather strongly indicates that μ''_{σ} does *indeed* diverge like the spe-

cific heat when $T \rightarrow T_c$. They dubbed this phenomenon a *Yang-Yang anomaly* [2]. Even though impurities in the propane system have definite effects on the heat-capacity data [5], the existence of a Yang-Yang anomaly cannot be ruled out and, in our assessment, remains the most plausible scenario. In fact, Orkoulas *et al.* [6] have performed grand canonical Monte Carlo simulations for the hard-core square-well fluid and concluded that this model system probably exhibits a negative but small Yang-Yang anomaly, i.e., a specific-heat-like divergence in the chemical potential derivative, $d^2 \mu_{\sigma}/dT^2$, of magnitude significantly less than the divergence of $v(d^2 p_{\sigma}/dT^2)$, where $v = V/N$. How can one then accommodate such a Yang-Yang anomaly in scaling theory?

The concept of asymptotic scaling has proved a powerful tool for gaining insight into critical phenomena in a variety of systems including fluids [7–12]. Furthermore, a scaling equation of state has been rather well confirmed experimentally for many fluids [13,14]. The currently accepted asymptotic scaling description of fluid criticality [15] requires two scaling fields, namely, a thermal field, \tilde{t} , and an ordering field, \tilde{h} , that, in leading order, are both linear combinations of $t \propto T - T_c$ and $h = \mu - \mu_c$, the deviations of the temperature and chemical potential from their critical values. This description has also been extended to describe fluctuations in finite systems and applied to estimating the critical points of model fluids [16]. However, within this scaling description, the chemical potential is always analytic along the phase boundary and through the critical point, thereby having a *finite* value of the second temperature derivative, μ''_{σ} . Hence, in order to account for a Yang-Yang anomaly, the current scaling description must be modified. Indeed, Fisher and Orkoulas [2] argued that the pressure deviation, $p - p_c$, must mix into the scaling fields, especially into the ordering field \tilde{h} .

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In order to formulate a scaling theory in which the pressure is mixed into the scaling fields, let us consider a *full thermodynamic description* of a one-component fluid as provided by a functional relation between the three thermodynamic fields, pressure, p , chemical potential, μ , and temperature, T , say

$$Y(p, \mu, T) = 0. \quad (1.2)$$

Extending the approach sketched in Ref. [2] to include the full spectrum of correction exponents (see also [17,18]) one may formulate a rather general scaling hypothesis by asserting that near a typical critical point, (p_c, μ_c, T_c) , the thermodynamics can be described, at least asymptotically, by

$$\Psi(\lambda^{2-\alpha}\tilde{p}, \lambda\tilde{t}, \lambda^\Delta\tilde{h}; \lambda^{-\theta_4}u_4, \lambda^{-\theta_5}u_5, \dots) = 0, \quad (1.3)$$

where λ is a free, positive scaling parameter. In this expression $\tilde{p}(p, \mu, T)$, $\tilde{t}(p, \mu, T)$, and $\tilde{h}(p, \mu, T)$ are the three relevant *nonlinear scaling fields*, while $u_4(p, \mu, T)$ and $u_5(p, \mu, T)$ are the leading even and odd irrelevant scaling fields, respectively. Including the quadratic nonlinear terms, we may write the basic nonlinear fields as

$$\begin{aligned} \tilde{p} &= \check{p} - k_0 t - l_0 \check{\mu} - r_0 t^2 - q_0 \check{\mu}^2 - v_0 t \check{\mu} \\ &\quad - m_0 \check{p}^2 - n_0 \check{p} t - n_3 \check{p} \check{\mu} + O_3(t, \check{\mu}, \check{p}), \end{aligned} \quad (1.4)$$

$$\begin{aligned} \tilde{t} &= t - l_1 \check{\mu} - j_1 \check{p} - r_1 t^2 - q_1 \check{\mu}^2 - v_1 t \check{\mu} \\ &\quad - m_1 \check{p}^2 - n_1 \check{p} t - n_4 \check{p} \check{\mu} + O_3(t, \check{\mu}, \check{p}), \end{aligned} \quad (1.5)$$

$$\begin{aligned} \tilde{h} &= \check{\mu} - k_1 t - j_2 \check{p} - r_2 t^2 - q_2 \check{\mu}^2 - v_2 t \check{\mu} \\ &\quad - m_2 \check{p}^2 - n_2 \check{p} t - n_5 \check{p} \check{\mu} + O_3(t, \check{\mu}, \check{p}), \end{aligned} \quad (1.6)$$

where we have introduced the dimensionless critical deviations [2]

$$t \equiv \frac{T - T_c}{T_c}, \quad \check{\mu} \equiv \frac{\mu - \mu_c}{k_B T_c}, \quad \check{p} \equiv \frac{p - p_c}{\rho_c k_B T_c}, \quad (1.7)$$

in which ρ_c is the critical (number) density and k_B is Boltzmann's constant, while $O_m(x, y, z)$ denotes a formal expansion in powers $x^j y^k z^l$ with $j + k + l \geq m$. In accepting these expansions we are neglecting any scaling-exponent “resonances” that might complicate the expressions by introducing logarithmic factors, etc., [19–22]. For ($d=3$)-dimensional systems, particularly real asymmetric fluids—which are of especial interest—this should be quite satisfactory. The irrelevant scaling fields, u_4, u_5, \dots , will, in general, have similar expansions in powers of the variables, $t, \check{\mu}$ and \check{p} .

As usual, α in (1.3) is the universal critical exponent of the specific heat and Δ is the gap exponent that is related to α and the exponents β (for the spontaneous magnetization), γ (for the susceptibility), and δ (for the critical isotherm) by the scaling relations

$$\Delta = 2 - \alpha - \beta = \beta + \gamma = \beta\delta, \quad (1.8)$$

while $\theta_4 \equiv \theta$ and θ_5 are the *positive* leading correction-to-scaling exponents. In the case of the ($d=3$)-dimensional Ising universality class, which is believed to characterize fluid criticality rather generally, we may accept $\alpha \approx 0.109$, $\beta \approx 0.326$, $\gamma \approx 1.239$, $\Delta \approx 1.565$, $\theta \approx 0.52$, and $\theta_5 \approx 1.32$ [17]. Finally, substituting $\lambda = 1/|\tilde{t}|$ into (1.3) yields the “thermal scaling” form

$$\Phi^\pm(\tilde{p}/|\tilde{t}|^{2-\alpha}, \tilde{h}/|\tilde{t}|^\Delta; u_4|\tilde{t}|^\theta, u_5|\tilde{t}|^{\theta_5}, \dots) = 0, \quad (1.9)$$

where $\Phi^\pm(x, y; \dots) = \Psi(x, \pm 1, y; \dots)$ in which \pm corresponds to $\tilde{t} \gtrless 0$.

A further observation is worth mentioning at this point. Specifically, if the critical point is drawn out into a lambda line without changing the universality class, by, e.g., the imposition of a magnetic field, H , or the addition of a second molecular component with chemical potential, say μ^{II} , etc., the only change needed in the formulation is the inclusion of a further, *nonordering field* g [$\propto H$ or $z_{\text{II}} = \exp(-\mu^{\text{II}}/k_B T)$, etc.] in the expansions of the three nonlinear scaling fields; likewise for any further fields that leave the universality class unaltered: see, e.g., [17,18].

Now the particle number N , volume V , and the entropy S are related by the Gibbs-Duhem relation

$$Vdp - SdT - Nd\mu = 0. \quad (1.10)$$

Hence the number density and the entropy density are given by

$$\rho \equiv \frac{N}{V} = \left(\frac{\partial p}{\partial \mu} \right)_T, \quad S \equiv \frac{S}{V} = \left(\frac{\partial p}{\partial T} \right)_\mu. \quad (1.11)$$

Other thermodynamic quantities, such as the specific heat, compressibility, etc., follow in the standard way.

The crucial point about the scaling formulation presented here is that the three standard thermodynamic fields, p, μ , and T , enter in a fully symmetrical way with no *a priori* assumptions as to which pair combination or thermodynamic potential, say $p(\mu, T)$ or $\mu(p, T)$, is “more basic.” By contrast, previous formulations have typically concluded that it was most appropriate to regard $p(\mu, T)$ as the “basic” quantity [15,17]. This is what one is led to by studying the standard lattice gases and what arises most naturally from field-theoretic and renormalization group approaches [20–22]. However, one might note that the original Widom formulation [7] was based on integrating the equation of state and led, fairly naturally, to a scaling hypothesis for the Helmholtz free energy density $f(\rho, T)$; on the other hand, the exactly soluble cluster-interaction fluids of Fisher and Felderhof [23] showed that $\mu(p, T)$ was the appropriate thermodynamic potential for describing critical-point scaling in these models.

It is easily seen, however, that the previous $p(\mu, T)$ formulation [15,17] is recaptured here simply by suppressing the \check{p} dependence in the nonlinear scaling fields \tilde{h} and \tilde{t} : i.e., in linear order, by setting $j_1 = j_2 = 0$ in (1.5) and (1.6), and in quadratic order, by setting $m_0 = m_1 = \dots = n_5 = 0$. In that

case the expansion of \tilde{p} in (1.4) merely serves to represent the usual “smooth background” $p_0(\mu, T)$ that is always required.

The original discussion of scaling in fluids [7,8] had to incorporate in the definition of the *ordering field* \tilde{h} the *mixing coefficient* k_1 which, indeed, is then directly proportional to $(d\mu_\sigma/dT)_c$ where $\mu_\sigma(T)$ represents the phase boundary below T_c ; but the coefficients j_1 , j_2 , and l_1 did not appear. Studies of various models later revealed that the coefficient l_1 , which mixes the chemical potential into the *thermal scaling field*, \tilde{t} , should also be included: doing so yielded an unexpected singularity in the coexistence curve diameter, $\bar{\rho}(T)$, proportional to $|t|^{1-\alpha}$. (See, e.g., Ref. [15].) Nevertheless, it was still argued (in Ref. [15]) that one could suppress the linear pressure mixing coefficients j_1 and j_2 despite the existence of soluble models in which scaling, in fact, required them [23].

It is only the recent reconsideration of the possibility of a Yang-Yang anomaly in real fluids and nonsymmetric models [2,5] that has led to the realization that *pressure mixing*, i.e., nonvanishing coefficients j_1 and j_2 in (1.5) and (1.6), should be reconsidered. Indeed, as shown in Ref. [2], if a nonvanishing Yang-Yang anomaly arises, so that $(d^2\mu_\sigma/dT^2)$ diverges when $T \rightarrow T_c^-$, then, within a scaling formulation, one must have $j_2 \neq 0$. In fact, that also leads, as we demonstrate below, to a singular term varying as $|t|^{2\beta}$ in the coexistence curve diameter, $\bar{\rho}(T)$, which, in realistic situations, will actually dominate the previously discovered $|t|^{1-\alpha}$ term [2,15]. Conversely, the absence of pressure mixing in the linear ordering field, i.e., $j_2=0$, implies the *absence* of a Yang-Yang anomaly as is the case for the standard lattice gases. Granted that j_2 may not vanish, it is clearly appropriate to allow $j_1 \neq 0$, i.e., to consider pressure mixing also in the thermal field, \tilde{t} .

In light of this background the aim of the analysis presented in this paper is to thoroughly explore the implications of the “complete scaling hypothesis” embodied in the relations (1.3)–(1.9). Hence in Sec. II the “complete scaling” theory is formulated with the incorporation of pressure mixing as well as corrections to scaling. For this purpose, we mostly follow the treatment given in Ref. [17]. The properties of the scaling functions in the two limiting cases, $\tilde{h}/\tilde{t}^\Delta \rightarrow 0$ or ∞ , are set out as well as the consequences of thermodynamic convexity or the Second Law of Thermodynamics [24]. For use in the subsequent calculations, generalized scaling densities and susceptibilities are defined and the relations between them and the actual physical quantities are determined.

Once the formulation of the scaling theory is completed, we examine, in Sec. III, the standard singular thermodynamic properties including the coexistence curve and the specific heat. We explicitly determine the nature of the phase boundaries, $p_\sigma(T)$ and $\mu_\sigma(T)$, of the coexistence curve diameter, $\bar{\rho} = \frac{1}{2}(\rho_{\text{liq}} + \rho_{\text{vap}})$ and of the half-jump, $\Delta\rho = \frac{1}{2}(\rho_{\text{liq}} - \rho_{\text{vap}})$, as well as of entropies at the coexistence curve. As mentioned above, the pressure-mixing coefficient j_2 generates a singular $|t|^{2-\alpha}$ term in the phase boundary $\mu_\sigma(T)$ and

thereby, the divergence of the $(d^2\mu_\sigma/dT^2)$ at the critical point: see Sec. III A; in addition, a singular $|t|^{2\beta}$ term in the coexistence curve diameter appears and dominates the $|t|^{1-\alpha}$ term known previously [15]: see Sec. III B. Furthermore, as demonstrated in Sec. III C, pressure mixing induces a strong, $\sim |t|^\beta$, singularity in the asymmetry ratio that measures the relative difference between the compressibilities/susceptibilities on the two sides of the co-existence curve.

In Sec. III D the linear mixing coefficients j_1, j_2, \dots, l_1 are related to various physical amplitudes, etc., which can, in principle, be measured via experiments or simulations. The Yang-Yang anomaly, which was the main motivation for this study, is discussed in Sec. III E; it is shown that the strength of the anomaly, namely \mathcal{R}_μ , which measures the contribution of the chemical potential to the heat capacity relative to that of the pressure in an asymptotic limit—see (1.1)—is related solely to the pressure-mixing coefficient j_2 .

In Sec. IV we study a number of special loci, particularly in the density-temperature (ρ, T) plane, that intersect the critical point. These loci are of interest in their own right but they prove to be especially useful in attempting to estimate precise values of the critical density, ρ_c , both in the case of real asymmetric fluids and in the simulation of various model systems such as the hard-core square-well fluid [6] and, more challengingly, primitive model electrolyte systems [25]. More concretely, we study the locus $\mu = \mu_c$, dubbed the *critical isokyme*, the critical isobar ($p = p_c$), the critical isotherm ($T = T_c$), and the critical isochore ($\rho = \rho_c$) in the (ρ, T) , (μ, T) , (ρ, T) , etc., planes. The singular exponents characterizing these loci are obtained and the corresponding amplitudes are expressed in terms of the mixing coefficients and the expansion coefficients of the scaling functions and, thereby, related to one another. One discovers, however, that these characterizations of the various loci may not be helpful in estimating the critical point in practical applications to experiments or simulations, since various critical parameter values must be known *a priori*; but, except for exactly soluble models, the requisite values are not normally available.

Hence, for direct applications to the analysis of simulation data, we also study in Sec. IV E, the “*k*-inflection loci” introduced by Orkoulas *et al.* [6]. The “*k*-susceptibility loci” are defined by the points of isothermal maxima of the modified susceptibility $\chi^{(k)} = \chi/\rho^k$ above T_c in the (ρ, T) plane where $\chi = \rho^2 k_B T K_T$ is the standard isothermal susceptibility while K_T is the compressibility. We find that these loci have leading $|t|^{2\beta}$ terms followed by more slowly varying $|t|^{1-\alpha}$ and t contributions: however, the leading amplitude *vanishes* when k takes some “optimal value” k_{opt} . Thus, when $k = k_{\text{opt}}$, the corresponding k locus “points” most directly to the critical point. Furthermore, we find that k_{opt} is directly related to the strength of the Yang-Yang anomaly via $k_{\text{opt}} = 3\mathcal{R}_\mu$. With the aid of simulations we illustrate these loci quantitatively for the hard-core square-well fluid and the restricted primitive model electrolyte, and compare the results with those for a van der Waals fluid: see Figs. 1–3, below.

One may, similarly [26], define “*k*-heat-capacity loci” via the points of isothermal maxima in the (ρ, T) plane of the

modified specific heat $C_V^{(k)} \equiv C_V/\rho^k$. These loci have not been used in past simulations but may be useful in the future. We find, as for the susceptibility loci, that a leading $|t|^{2\beta}$ term appears in the near-critical expansions, followed by $|t|^{1-\alpha}$ and t terms. Again, the leading amplitude vanishes when k is equal to a special value that is once more related directly to the Yang-Yang anomaly: see Sec. IV F.

In order to provide semiquantitative guides to the behavior of these loci in real systems, we study them in Sec. V, using classical theory for the gas-liquid phase transition on the basis of a Landau order-parameter expansion of the free energy. We obtain the vapor pressure, $p_\sigma(T)$, and the saturation chemical potential, $\mu_\sigma(T)$, up to second order in t , while in the current literature they appear only up to first order [13]. The coexistence curve diameter, $\bar{\rho}(T)$, is also found to order t . These curves can be analytically continued from $T \leq T_c$ to the one-phase region above T_c so providing special loci that cannot, in general, be defined in nonclassical cases. Using the van der Waals equation, these analytic extensions are illustrated quantitatively: see Figs. 5 and 6. In addition to these critical loci, the k -susceptibility loci are obtained and compared with those of the hard-core square-well [6] and the restricted primitive model [25]. In Sec. V D the Yang-Yang relation (1.1) is discussed in more detail within classical theory (see Fig. 7) and extended to general loci in the (ρ, T) plane. A Yang-Yang-type relation along the critical isotherm is discussed briefly.

Section VI summarizes the paper and provides a key to the main results. Some further details are provided in the Appendix and others are available in the first author's thesis [26].

II. SCALING FORMULATION AND THERMODYNAMIC FUNCTIONS

To explore the scaling description (1.9), it is appropriate to focus on the relevant scaling variable (or combination)

$$y(\check{p}, \check{\mu}, t) = U\check{h}/|\check{t}|^\Delta, \quad (2.1)$$

where, without loss of generality, U may be taken as a positive constant. The basic reason for this choice, as against $\check{p}/|\check{t}|^{2-\alpha}$, is that Δ is, in general, less than $(2-\alpha)$ [since, see (1.8), $\beta > 0$] so that y diverges less rapidly when $t \rightarrow 0$. Beyond y we need to account for the full set of irrelevant scaled variables, namely,

$$y_k(\check{p}, \check{\mu}, t) = U_k \check{h}(\check{p}, \check{\mu}, t) |\check{t}|^{\theta_k}, \quad (2.2)$$

$$\theta_{k+1} \geq \theta_k > 0, \quad k = 4, 5, \dots,$$

where $U_k \propto u_k$ and we will assume, when needed, that the associated irrelevant amplitudes U_k are noncritical, meaning that $U_k(\check{p}, \check{\mu}, t)$ can be expanded in a formal power series of \check{p} , $\check{\mu}$ and t (which may not necessarily converge). Since a fluid has, in general, no obvious symmetry, we do *not* impose any restriction on the U_k : but see also the discussion in Ref. [17] Sec. II.

Now the thermodynamic potential for the fluid (in this case the pressure—as a consequence of selecting y as the primary scaled variable) can be written by formally solving (1.9) as

$$\tilde{p} = Q |\check{t}|^{2-\alpha} W_\pm(y, y_4, y_5, \dots), \quad (2.3)$$

where Q is a positive amplitude while W_\pm is a scaling function that, in the case of bulk fluids, embodies the properties of the $(d=3)$ -dimensional Ising universality class. In this expression the subscript \pm refers to $\tilde{t} \gtrless 0$. On choosing appropriate values for Q and U , the scaling function, $W_\pm(y, \dots)$ becomes universal. Note that the usual analytic background part of the potential, say $p_0(t, \check{\mu})$, is included in the nonlinear scaling field \tilde{p} : see (1.4) which may, clearly, be solved iteratively for \check{p} to yield an expansion for $p_0(t, \check{\mu})$.

A. Scaling functions

The scaling function $W_\pm(y, y_4, y_5, \dots)$ should be both universal and invariant under change of sign of the odd arguments y, y_5, y_7, \dots . Since the irrelevant scaling variables, y_4, y_5, \dots , vanish as the critical point is approached, we can also expand the scaling function W_\pm as [17]

$$W_\pm(y, y_4, y_5, \dots) = W_\pm^0(y) + y_4 W_\pm^{(4)}(y) + y_5 W_\pm^{(5)}(y) + \dots$$

$$+ y_4^2 W_\pm^{(4,4)}(y) + y_4 y_5 W_\pm^{(4,5)}(y) + \dots$$

$$= \sum_{\kappa} W_\pm^{\kappa}(y) y^{|\kappa|}, \quad (2.4)$$

where for brevity we have used the multi-index, κ , defined via

$$\kappa = 0, (4), (5), \dots, (4,4), (4,5), \dots, (4,4,4), \dots, \quad (2.5)$$

as a label and as an exponent via

$$y^0 \equiv 1, \quad y^{[i,j,\dots,n]} \equiv y_i y_j \dots y_n. \quad (2.6)$$

We consider $\kappa = (i, j, \dots, n)$ to be odd or even according to whether the sum $i + j + \dots + n$ is odd or even. The symmetry of $W_\pm(y, y_4, y_5, \dots)$ then requires [17]

$$W_\pm^{\kappa}(-y) = (-)^{\kappa} W_\pm^{\kappa}(y). \quad (2.7)$$

Recognizing this symmetry, one may write expansions for $W_\pm^{\kappa}(y)$ for small y . For $\tilde{t} > 0$ we have

$$W_+^{\kappa}(y) = W_+^{\kappa} + y^2 W_+^{\kappa} + y^4 W_+^{\kappa} + \dots \quad \text{for } \kappa \text{ even,}$$

$$= y W_+^{\kappa} + y^3 W_+^{\kappa} + y^5 W_+^{\kappa} + \dots \quad \text{for } \kappa \text{ odd.} \quad (2.8)$$

By choosing appropriate values for the nonuniversal metric amplitudes Q, U , etc., the expansion coefficients can be normalized, in general, such that [17,24]

$$W_{+2}^0 = W_{+0}^{\kappa} = 1 \quad (\kappa \text{ even}) \quad \text{or} \quad W_{+1}^{\kappa} = 1 \quad (\kappa \text{ odd}). \quad (2.9)$$

For $\tilde{t} < 0$, the existence of the first-order transition leads to $|y|$ factors in the expansions so that one has [17]

$$W_{\pm}^{\kappa}(y) = [W_{-0}^{\kappa} + |y|W_{-1}^{\kappa} + y^2W_{-2}^{\kappa} + |y|^3W_{-3}^{\kappa} + \dots] \sigma_{\kappa}(y), \quad (2.10)$$

where the special signum function is defined by

$$\begin{aligned} \sigma_{\kappa}(y) &= 1 && \text{for } \kappa \text{ even,} \\ &= \text{sgn}(y) && \text{for } \kappa \text{ odd.} \end{aligned} \quad (2.11)$$

Thermodynamic convexity (which embodies the Second Law) then requires that W_{-1}^0 and W_{-2}^0 must both be positive: see Ref. [24].

For large arguments, $|y| \rightarrow \infty$, the scaling functions $W_{+}^{\kappa}(y)$ and $W_{-}^{\kappa}(y)$ must satisfy stringent matching conditions to ensure the analyticity of the potential through the plane $\tilde{t} = 0$ for all $\tilde{h} \neq 0$. By these conditions, the functions $W_{\pm}^{\kappa}(y)$ may be written as

$$W_{\pm}^{\kappa}(y) \approx W_{\infty}^{\kappa} |y|^{(2-\alpha+\theta[\kappa])/\Delta} \left[1 + \sum_{l=1}^{\infty} (\pm)^l w_l^{\kappa} |y|^{-l/\Delta} \right] \sigma_{\kappa}(y), \quad (2.12)$$

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

$$\theta[0] \equiv 0, \quad \theta[(i, j, \dots, n)] = \theta_i + \theta_j + \dots + \theta_n, \quad (2.13)$$

with $i, j, \dots, n \geq 4$. By virtue of the normalizations (2.9) the numerical amplitudes W_{-j}^{κ} , W_{+j}^{κ} , W_{∞}^{κ} , and w_l^{κ} should all be universal. Beyond that, thermodynamic convexity dictates that W_{∞}^0 and w_0^0 must be positive while $(w_1^0)^2/w_2^0$ must be bounded above [24]. The sign of w_1^0 is not determined by convexity alone but must, in general, be negative: see Ref. [24]. This plays an important role in determining allowable phase diagrams in a density (or composition) space at critical end points [17,24].

B. Generalized density and entropy

To extract explicit results from (2.3) revealing the singularities of the various thermodynamic derivatives, critical loci, etc., we first recall (1.11) and define a dimensionless reduced density, $\check{\rho}$, and entropy, \check{s} , by

$$\check{\rho} \equiv \frac{\rho}{\rho_c} = \left(\frac{\partial \check{p}}{\partial \check{\mu}} \right)_t, \quad \check{s} \equiv \frac{\mathcal{S}}{\rho_c k_B} = \left(\frac{\partial \check{p}}{\partial t} \right)_{\check{\mu}}. \quad (2.14)$$

Similarly, the generalized number density, $\tilde{\rho}$, and entropy density, \tilde{s} , will be defined by

$$\tilde{\rho} \equiv \left(\frac{\partial \tilde{p}}{\partial \tilde{h}} \right)_{\tilde{t}}, \quad \tilde{s} \equiv \left(\frac{\partial \tilde{p}}{\partial \tilde{t}} \right)_{\tilde{h}}. \quad (2.15)$$

These quantities then obey the usual simple scaling rules, namely, $\tilde{\rho} \sim |\tilde{t}|^{\beta}$ and $\tilde{s} \sim |\tilde{t}|^{1-\alpha}$ when $\tilde{t} \rightarrow 0$.

To find concrete expressions for $\check{\rho}$ and \check{s} , one may consider the differential relation,

$$d\tilde{p} = \tilde{\rho} d\tilde{h} + \tilde{s} d\tilde{t}, \quad (2.16)$$

where it is appropriate to recall that all the scaling variables y_k in (2.3) are functions (only) of \check{p} , $\check{\mu}$, and t and, hence, of $\tilde{\rho}$, $\tilde{\mu}$, and \tilde{t} . Using (1.4)–(1.6), this differential relation may be written as

$$\begin{aligned} (1 - 2m_0\check{\rho} - n_0\check{\mu} - n_3t + j_2\tilde{\rho} + j_1\tilde{s} + \dots) d\check{\rho} \\ = (l_0 + n_0\check{\rho} + 2q_0\check{\mu} + v_0t + \tilde{\rho} - l_1\tilde{s} + \dots) d\check{\mu} \\ + (k_0n_3\check{\rho} + v_0\check{\mu} + 2r_0t + \tilde{s} - k_1\tilde{\rho} + \dots) dt, \end{aligned} \quad (2.17)$$

where in the brackets we have retained only terms up to linear order. Using (2.14), we then obtain the relations

$$\check{\rho} = \frac{l_0 + n_0\check{\rho} + 2q_0\check{\mu} + v_0t + \tilde{\rho} - l_1\tilde{s} + \dots}{1 - 2m_0\check{\rho} - n_0\check{\mu} - n_3t + j_2\tilde{\rho} + j_1\tilde{s} + \dots}, \quad (2.18)$$

$$\check{s} = \frac{k_0 + n_3\check{\rho} + v_0\check{\mu} + 2r_0t + \tilde{s} - k_1\tilde{\rho}}{1 - 2m_0\check{\rho} - n_0\check{\mu} - n_3t + j_2\tilde{\rho} + j_1\tilde{s} + \dots}. \quad (2.19)$$

If the *nonlinear mixing coefficients* m_j , n_j , \dots , v_j in (1.4)–(1.6) are ignored, these expressions may be approximated by

$$\check{\rho} \approx \frac{l_0 + \tilde{\rho} - l_1\tilde{s}}{1 + j_2\tilde{\rho} + j_1\tilde{s}}, \quad \check{s} \approx \frac{k_0 + \tilde{s} - k_1\tilde{\rho}}{1 + j_2\tilde{\rho} + j_1\tilde{s}}. \quad (2.20)$$

Note that $\check{\rho}$ and \check{s} are *nonlinear* functions of $\tilde{\rho}$ and \tilde{s} owing to the pressure-mixing coefficients, j_1 and j_2 . In the absence of pressure mixing (i.e., $j_1 = j_2 = 0$), we recover the Bruce-Wilding *linear* relations [16]. We will see later that the approximation (2.20) is adequate to derive the most important singularities in leading order.

C. Generalized susceptibilities

The second derivatives of the potential determine the usual response functions, e.g., susceptibilities, heat capacities, etc. We define the basic reduced susceptibilities

$$\begin{aligned} \check{\chi}_{NN} &\equiv (\partial^2 \check{p} / \partial \check{\mu}^2)_t, & \check{\chi}_{UU} &\equiv (\partial^2 \check{p} / \partial t^2)_{\check{\mu}}, \\ \check{\chi}_{NU} &\equiv (\partial^2 \check{p} / \partial \check{\mu} \partial t) = (\partial^2 \check{p} / \partial t \partial \check{\mu}). \end{aligned} \quad (2.21)$$

These are related to the number and energy fluctuations most directly accessible in grand canonical simulations [6]. The isothermal susceptibility χ is defined by

$$\chi \equiv (\partial \rho / \partial \mu)_T = (\partial^2 p / \partial \mu^2)_T, \quad (2.22)$$

and is related to the isothermal compressibility, $K_T = \rho^{-1}(\partial \rho / \partial p)_T$, by $\chi = \rho^2 K_T$ and to the reduced susceptibility $\check{\chi}_{NN}$ by

$$\chi = (\rho_c / k_B T_c) \check{\chi}_{NN}. \quad (2.23)$$

Experimentally, the most important heat capacity for fluids is the constant-volume heat capacity with a density defined by

$$C_V = \frac{T}{\rho} \left(\frac{\partial S}{\partial T} \right)_\rho, \quad (2.24)$$

where S is the entropy density defined in (1.11). It is convenient to introduce the dimensionless reduced specific heat, namely,

$$\check{C}_V \equiv (\partial \check{s} / \partial t)_\rho, \quad (2.25)$$

for which one has

$$\rho C_V / T = (k_B \rho_c / T_c) \check{C}_V. \quad (2.26)$$

The reduced specific heat, \check{C}_V , is then related to the reduced susceptibilities in (2.21) via [6]

$$\check{C}_V = \check{\chi}_{UU} - \check{\chi}_{NU}^2 / \check{\chi}_{NN}. \quad (2.27)$$

Finally, we define generalized (scaling) susceptibilities via

$$\tilde{\chi}_{hh} \equiv \left(\frac{\partial^2 \tilde{p}}{\partial \tilde{h}^2} \right)_{\tilde{t}}, \quad \tilde{\chi}_{tt} \equiv \left(\frac{\partial^2 \tilde{p}}{\partial \tilde{t}^2} \right)_{\tilde{h}}, \quad \tilde{\chi}_{ht} \equiv \left(\frac{\partial^2 \tilde{p}}{\partial \tilde{h} \partial \tilde{t}} \right). \quad (2.28)$$

From (2.3) one finds $\tilde{\chi}_{hh} \sim |\tilde{t}|^{-\gamma}$, $\tilde{\chi}_{ht} \sim |\tilde{t}|^{\beta-1}$, and $\tilde{\chi}_{tt} \sim |\tilde{t}|^{-\alpha}$ when $\tilde{t} \rightarrow 0$. When the nonlinear mixing terms in the scaling fields are ignored, as above, $\check{\chi}_{NN}$ can be expressed in terms of the generalized densities and susceptibilities as

$$\check{\chi}_{NN} \approx \frac{(e_1 + e_2 \tilde{s})^2 \tilde{\chi}_{hh} + (e_3 + e_2 \tilde{\rho})^2 \tilde{\chi}_{tt} - 2(e_1 + e_2 \tilde{s})(e_3 + e_2 \tilde{\rho}) \tilde{\chi}_{ht}}{(1 + j_2 \tilde{\rho} + j_1 \tilde{s})^3}, \quad (2.29)$$

where the derived mixing coefficients are

$$e_1 = 1 - j_2 l_0, \quad e_2 = j_1 + j_2 l_1, \quad e_3 = l_1 + j_1 l_0. \quad (2.30)$$

The detailed derivation of (2.29) is presented in Appendix F of Ref. [26] henceforth to be denoted **K**; there it is also shown how (2.29) [**K**(3.41)] captures the leading singular correction terms.

III. THERMODYNAMIC PROPERTIES

A. Phase boundaries

The phase boundaries, say $p_\sigma(T)$ and $\mu_\sigma(T)$ [or $\check{p}_\sigma(t)$ and $\check{\mu}_\sigma(t)$], on which two phases may coexist, can be determined by equating the pressure and chemical potential on the vapor and liquid sides below T_c (i.e., for $\tilde{t} < 0$). On using the small- y expansion of \tilde{p} for $\tilde{t} < 0$ with the aid of (2.10), we obtain (including higher order terms)

$$\begin{aligned} \tilde{p}_\pm = & Q |\tilde{t}|^{2-\alpha} [W_{-0}^0 \pm W_{-1}^0 y + W_{-2}^0 y^2 + \dots \\ & + U_{4c} |\tilde{t}|^\theta (W_{-0}^{(4)} \pm W_{-1}^{(4)} y + W_{-2}^{(4)} y^2 + \dots) \\ & \pm U_{5c} |\tilde{t}|^{\theta_5} (W_{-0}^{(5)} \pm W_{-1}^{(5)} y + W_{-2}^{(5)} y^2 + \dots) + \dots], \end{aligned} \quad (3.1)$$

where \pm now refers to $\tilde{h} \gtrless 0$, while U_{4c} and U_{5c} are the critical values of the irrelevant scaling amplitudes, U_4 and U_5 , respectively. Equating \tilde{p}_+ and \tilde{p}_- then yields

$$\begin{aligned} W_{-1}^0 y = & -W_{-0}^{(5)} U_{5c} |\tilde{t}|^{\theta_5} - W_{-1}^{(4)} U_{4c} |\tilde{t}|^\theta y \\ & - W_{-2}^{(5)} U_{5c} |\tilde{t}|^{\theta_5} y^2 + \dots, \end{aligned} \quad (3.2)$$

where one sees that various even and odd terms cancel. Solving for y iteratively, one obtains

$$y = -\frac{W_{-0}^{(5)}}{W_{-1}^0} U_{5c} |\tilde{t}|^{\theta_5} + \frac{W_{-1}^{(4)} W_{-0}^{(5)}}{(W_{-1}^0)^2} U_{4c} U_{5c} |\tilde{t}|^{\theta+\theta_5} + \dots. \quad (3.3)$$

Note that in contrast to the symmetric case (e.g., the ferromagnetic Ising model) where $U_5 = 0$, the scaling field does *not* vanish identically along the phase boundary. Using the definition (2.1), we find the phase boundary is given by

$$\tilde{h}_\sigma(\tilde{t}) = E_1 |\tilde{t}_\sigma|^{\Delta+\theta_5} + E_2 |\tilde{t}_\sigma|^{\Delta+\theta+\theta_5} + \dots, \quad (3.4)$$

where the coefficients are

$$E_1 = -\frac{U_{5c} W_{-0}^{(5)}}{U W_{-1}^0}, \quad E_2 = \frac{U_{4c} U_{5c} W_{-1}^{(4)} W_{-0}^{(5)}}{U (W_{-1}^0)^2}. \quad (3.5)$$

Now substituting $\mu = \mu_\sigma(T)$ and $p = p_\sigma(T)$ in (1.5) and (1.6) and using (3.4), we obtain an expansion [see **K**(3.65)] of the chemical-potential deviation

$$\check{\mu}_\sigma(T) = [\mu_\sigma(T) - \mu_c] / k_B T_c, \quad (3.6)$$

in powers of t , of $\check{\mu}_\sigma$ itself, and of

$$\check{p}_\sigma(T) = [p_\sigma(T) - p_c] / \rho_c k_B T_c. \quad (3.7)$$

One can solve this equation iteratively for $\check{\mu}_\sigma$ as a function of t and \check{p}_σ to obtain

$$\begin{aligned} \check{\mu}_\sigma(T) = & j_2 \check{p}_\sigma + k_1 t + (m_2 + j_2^2 q_2 + j_2 n_2) \check{p}_\sigma^2 + (r_2 + k_1 q_2 + v_2 k_1) t^2 + (n_5 + 2j_2 k_1 q_2 + k_1 n_2 + v_2 j_2) \check{p}_\sigma t \\ & + E_1 |(1 - k_1 l_1) t - (j_1 + j_2 l_1) \check{p}_\sigma|^{\Delta + \theta_5} + E_2 |(1 - k_1 l_1) t - (j_1 + j_2 l_1) \check{p}_\sigma|^{\Delta + \theta + \theta_5} + \dots \end{aligned} \quad (3.8)$$

Substituting this result into (1.4) yields

$$\tilde{p}_\sigma = (1 - j_2 l_0) \check{p}_\sigma - (k_0 + k_1 l_0) t - \tilde{E}_1 \check{p}_\sigma^2 - \tilde{E}_2 t^2 - \tilde{E}_3 \check{p}_\sigma t + \dots, \quad (3.9)$$

where the coefficients \tilde{E}_j depend on the *quadratic* nonlinear-field coefficients r_0, m_0, \dots in (1.4) to (1.6): see **K**(3.68)–(3.70).

Similarly, from (1.5) and (3.8), one finds

$$\tilde{t}_\sigma = (1 - k_1 l_1) t - (j_1 + j_2 l_1) \check{p}_\sigma + \dots \quad (3.10)$$

Substituting this into (3.1) with the aid of (2.1) and (3.4), combining it with (3.9), and solving iteratively for \check{p}_σ finally yields the result

$$\begin{aligned} \check{p}_\sigma(T) = & \check{p}_{\sigma,1} t + \check{p}_{\sigma,2} t^2 + A_p |t|^{2-\alpha} [1 + a_p |t|^\theta + \dots \\ & + b_p |t|^{\theta_5 - \beta} + a'_p |t|^{\theta_5 - \beta + \theta} + \dots \\ & + b'_p |t|^{2\theta_5} + \dots] + \dots, \end{aligned} \quad (3.11)$$

where the leading coefficients are given by

$$\check{p}_{\sigma,1} = \frac{k_0 + k_1 l_0}{1 - j_2 l_0}, \quad \check{p}_{\sigma,2} = \tilde{E}_1 \check{p}_{\sigma,1}^2 + \tilde{E}_2 + \tilde{E}_3 \check{p}_{\sigma,1}, \quad (3.12)$$

$$\begin{aligned} A_p = & \frac{Q W_{-0}^0}{1 - j_2 l_0} |\tau|^{2-\alpha}, \quad a_p = \frac{U_{4c} W_{-0}^{(4)}}{W_{-0}^0} |\tau|^\theta, \\ b_p = & \frac{l_0 (1 - j_2 l_0) E_1}{Q W_{-0}^0} |\tau|^{\theta_5 - \beta}, \end{aligned} \quad (3.13)$$

in which we have introduced the mixing factor

$$\tau = 1 - k_1 l_1 - \check{p}_{\sigma,1} (j_1 + j_2 l_1), \quad (3.14)$$

while E_1 is given in (3.5) and a'_p and b'_p can be derived from **K**(3.74).

Note that the leading even correction-to-scaling term enters the phase boundary $p_\sigma(T)$ with an exponent $(2 - \alpha) + \theta$, while the odd correction-to-scaling term has an exponent $(2 - \alpha) - \beta + \theta_5$. In addition, it is not hard to see that the subsequent term $b_p |t|^{2\theta_5}$ (and analogous terms below) *must* be preceded by *lower order* terms such as $d_p |t|^{2\theta}$, $a''_p |t|^{\theta+1}$, $e_p |t|^{3\theta}$, $a'''_p |t|^{\theta+2}$, etc.

Now let us substitute the result (3.11) back into (3.8). With a little further effort, one obtains the desired result for the chemical potential on the phase boundary, namely,

$$\begin{aligned} \check{\mu}_\sigma(T) = & \check{\mu}_{\sigma,1} t + \check{\mu}_{\sigma,2} t^2 + A_\mu |t|^{2-\alpha} [1 + a_\mu |t|^\theta + \dots \\ & + b_\mu |t|^{\theta_5 - \beta} + a'_\mu |t|^{\theta_5 - \beta + \theta} + \dots + b'_\mu |t|^{2\theta_5} + \dots] \\ & + \dots, \end{aligned} \quad (3.15)$$

where the leading coefficients satisfy

$$\check{\mu}_{\sigma,1} = k_1 + j_2 \check{p}_{\sigma,1}, \quad A_\mu = j_2 A_p, \quad a_\mu = a_p, \quad (3.16)$$

$$b_\mu = E_1 |\tau|^{\Delta + \theta_5} / A_\mu, \quad a'_\mu = b_\mu c_p, \quad b'_\mu = b'_p, \quad (3.17)$$

while $\check{\mu}_{\sigma,2}$ is given in **K**(3.78).

As is to be expected, the spectrum of singular terms that appears in the expansion for $\mu_\sigma(T)$ is the same as that for $p_\sigma(T)$. Note, however, that the leading singular amplitude, A_μ , for $\mu_\sigma(T)$ is proportional to the pressure-mixing coefficient j_2 . Thus, in contrast to the traditional scaling treatment, pressure mixing in the scaling fields implies that the second derivative of $\mu_\sigma(T)$ diverges at the critical point with the same exponent α as the specific heat. However, even in the absence of pressure mixing *per se* the phase boundary $\mu_\sigma(T)$ is not analytic: rather its *third derivative diverges* (in contrast again to lattice-gas models) owing to the odd correction-to-scaling term, since in the case of fluids one has $2 < 2 - \alpha - \beta + \theta_5 = \Delta + \theta_5 < 3$. [Note that the amplitude, $A_\mu b_\mu$, of $|t|^{2-\alpha-\beta+\theta_5}$ in (3.15) does *not* vanish when $j_2 = 0$.] The conclusion that $\mu''_\sigma(T)$ exhibits a cusplike behavior near the critical point was originally advanced by Ley-Koo and Green [27] and enters into the analysis of the effects of impurities on the detection of the Yang-Yang anomaly [5]: see the discussion below in Sec. III E.

B. Densities and entropies at coexistence

The generalized densities along the phase boundary, $\tilde{\rho}_\sigma$ and \tilde{s}_σ , can be obtained from (2.3) and (2.15) by using the results (3.11) and (3.15) for \check{p}_σ and $\check{\mu}_\sigma$. After some algebra, we find

$$\begin{aligned} \tilde{\rho}_\sigma(t) \approx & \pm Q U |\tau t|^\beta [W_{-1}^0 + U_{4c} W_{-1}^{(4)} |\tau t|^\theta \pm U_{5c} \{W_{-1}^{(5)} \\ & - (W_{-2}^0 W_{-0}^{(5)} / W_{-1}^0)\} |\tau t|^{\theta_5} + \dots], \end{aligned} \quad (3.18)$$

$$\begin{aligned} \tilde{s}_\sigma(t) \approx & -Q |\tau t|^{1-\alpha} [(2 - \alpha) W_{-0}^0 + (2 - \alpha + \theta) U_{4c} W_{-0}^{(4)} |\tau t|^\theta \\ & \pm (\Delta + \theta_5) U_{5c} W_{-0}^{(5)} |\tau t|^{\theta_5} + \dots], \end{aligned} \quad (3.19)$$

where \pm refers to $\tilde{h} \geq 0$. Using (2.18) and (2.19) and expanding in powers of t , we finally obtain the number density and entropy density on the two sides of the coexistence curve as

$$\begin{aligned} \rho^\pm(T) = & \rho_c \{ 1 + A_{2\beta} |t|^{2\beta} + A_{1-\alpha} |t|^{1-\alpha} + A_1 t + \dots \\ & + A_5 |t|^{\beta+\theta_5} + \dots \pm B |t|^\beta [1 + b_\theta |t|^\theta \\ & + b_{2\beta} |t|^{2\beta} + \dots] \}, \end{aligned} \quad (3.20)$$

$$\begin{aligned} S^\pm(T) = & \rho_c k_B \{ k_0 + S_{2\beta} |t|^{2\beta} + S_{1-\alpha} |t|^{1-\alpha} + S_1 t + \dots \\ & + S_5 |t|^{\beta+\theta_5} + \dots \pm B_s |t|^\beta [1 + d_\theta |t|^\theta \\ & + d_{2\beta} |t|^{2\beta} + \dots] \}, \end{aligned} \quad (3.21)$$

where terms varying as $|t|^{\beta+1}$ and $|t|^{1-\alpha+\beta}$ have not been displayed and higher order terms such as $\pm |t|^{\beta+\Delta}$, $|t|^{\beta+2-\alpha}$, etc. will also be present in general. Implicit in these results is the conclusion

$$l_0 = \check{\rho}_c \equiv 1 \quad \text{and} \quad k_0 = \check{s}_c \equiv S_c / \rho_c k_B. \quad (3.22)$$

The leading coefficients for the density are then

$$B = (1 - j_2) Q U W_{-1}^0 |\tau|^\beta, \quad b_\theta = U_{4c} W_{-1}^{(4)} |\tau|^\theta / W_{-1}^0, \quad (3.23)$$

$$b_{2\beta} = j_2^2 B^2 / (1 - j_2)^2, \quad A_{2\beta} = -j_2 B^2 / (1 - j_2), \quad (3.24)$$

$$A_{1-\alpha} = (2 - \alpha)(l_1 + j_1) Q W_{-0}^0 |\tau|^{1-\alpha}, \quad (3.25)$$

$$A_1 = v_0 + n_3 + (2q_0 + n_0) \check{\mu}_{\sigma,1} + (n_0 + 2m_0) \check{p}_{\sigma,1}, \quad (3.26)$$

while the coefficients for the entropy satisfy

$$B_s / B = -(k_1 + j_2 k_0) / (1 - j_2), \quad d_\theta = b_\theta, \quad (3.27)$$

$$d_{2\beta} = j_2^2 B_s^2 / (k_1 + j_2 k_0)^2, \quad S_{2\beta} = -j_2 B_s^2 / (k_1 + j_2 k_0), \quad (3.28)$$

$$S_{1-\alpha} = (2 - \alpha)(j_1 k_0 - 1) Q W_{-0}^0 |\tau|^{1-\alpha},$$

$$S_5 = B_s A_5 / B, \quad (3.29)$$

and A_5 and S_5 follow from **K**(3.83), (3.84).

From (3.20) the coexistence curve diameter, $\bar{\rho}(T) = \frac{1}{2}[\rho_{\text{liq}}(T) + \rho_{\text{vap}}(T)]$, and the width, $2\Delta\rho(T) = \rho_{\text{liq}}(T) - \rho_{\text{vap}}(T)$, of the coexistence curve, follow immediately. As anticipated, we see that the diameter contains a $|t|^{2\beta}$ term that is proportional to the pressure-mixing coefficient j_2 ; and, since $2\beta < 1 - \alpha$ for typical fluids, this actually dominates the previously anticipated $|t|^{1-\alpha}$ term [15]. Likewise, one may read off the entropy diameter, $\bar{S}(T)$, and entropy jump, $\Delta S(T)$, from (3.21). Again one observes that the dominating $|t|^{2\beta}$ term in $\bar{S}(T)$ is proportional to j_2 .

The total entropy in the two-phase region is given by

$$S_\sigma^{\text{tot}}(T) = V \frac{dp_\sigma}{dT} - N \frac{d\mu_\sigma}{dT}. \quad (3.30)$$

On the critical isochore, $\rho = \rho_c$, this yields the entropy density

$$S_\sigma(T; \rho_c) = S_c + \rho_c k_B (1 - j_2) A_p |t|^{1-\alpha} + O(t) \quad (3.31)$$

from which, as was to be anticipated, the $|t|^{2\beta}$ terms have canceled. [Recall that A_p is defined in (3.13).]

In Fig. 1 grand canonical simulation data for the coexistence curve of the hard-core square-well fluid are presented. Adopting the critical point estimates, $T_c \approx 1.2179$ and $\rho_c \approx 0.3067$ [6], and the Ising values for the critical exponents yields the estimates $B = 1.2026_4$, $A_{2\beta} = -0.0007_3$, $A_{1-\alpha} = 0.189_7$, $A_1 = -0.0691_4$, $b_\theta = -0.257_6$, and $b_{2\beta} = -0.085_2$ for the amplitudes in (3.20) [6]. This fit is shown in Fig. 1 as a solid line that connects the coexisting density estimates (circles) to the critical point. Similarly, coexistence simulation data (in a $\zeta = 5$ fine discretization level) for the restricted primitive model electrolyte are presented in Fig. 2. The solid line—the Ising fit to the coexistence data—is drawn by adopting the critical point values, $T_c \approx 0.05069$, $\rho_c \approx 0.079$ [25] and the amplitude estimates, $B = 0.274$, $A_{2\beta} = 0.0165$, $A_{1-\alpha} = 0.919$, $A_1 = 0.586$, $b_\theta = 1.464$, and $b_{2\beta} = 2.254$. However, one must note that the specific numbers attached to these particular amplitude estimates *cannot* have a very significant meaning, unless the higher order corrections are considered more carefully than is practicable with the data currently available.

C. Susceptibilities at coexistence

The reduced susceptibility, $\check{\chi}_{NN}$ in (2.21), on the coexistence boundary is also of particular interest as we point out

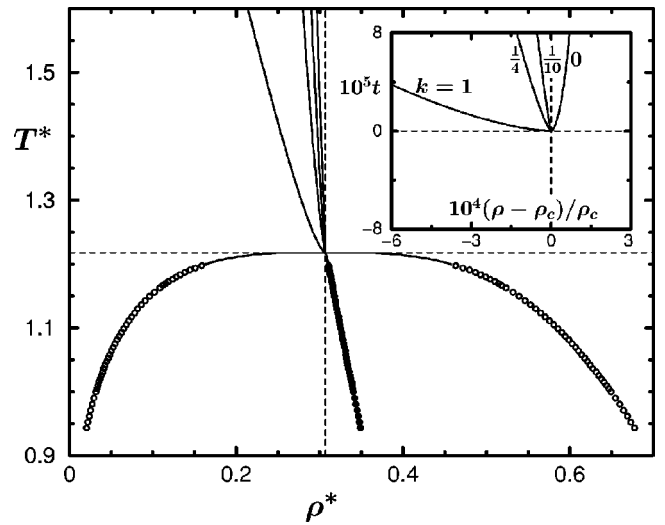


FIG. 1. Coexistence data (open circles, with closed circles for the diameter) for the hard-core square-well fluid obtained by Orkoulas *et al.* [6]. The solid lines connecting the data points represent an Ising-type fit: see Eq. (3.20). The vertical and horizontal dashed lines locate the critical isochore, $\rho^* = \rho_c^* \approx 0.3067$, and the critical isotherm, $T^* = T_c^* \approx 1.2179$ [6]. The curves above criticality and in the inset depict estimates for the k -susceptibility loci for the values of k indicated; but note that the $k=0$ locus curls back to lower values of the density as T rises.

here. Using (3.11) and (3.15) for \check{p}_σ and $\check{\mu}_\sigma$, the generalized susceptibilities on the phase boundary, $\tilde{\chi}_{hh,\sigma}$ and $\tilde{\chi}_{ht,\sigma}$, can be obtained from (2.3) and (2.28). After some algebra, we find

$$\tilde{\chi}_{hh,\sigma} \approx 2QU^2|\tau t|^{-\gamma} [W_{-2}^0 + U_{4c}W_{-2}^{(4)}|\tau t|^\theta \pm U_{5c}\{W_{-2}^{(5)} - 3(W_{-3}^0W_{-0}^{(5)}/W_{-1}^0)\}|\tau t|^{\theta_5} + \dots], \quad (3.32)$$

$$-\tilde{\chi}_{ht,\sigma} \approx \pm \beta QUW_{-1}^0|\tau t|^{\beta-1} + \dots, \quad (3.33)$$

where \pm refers to $\tilde{h} \gtrless 0$, while $\tilde{\chi}_{ht,\sigma}$ enters $\tilde{\chi}_{NN}$ only as a higher order correction. On substituting these results and (3.18) and (3.19) into (2.29), we obtain the reduced susceptibility on the two sides of the coexistence curve as

$$\begin{aligned} \check{\chi}_{NN}^\pm(T) = & C^-|t|^{-\gamma}\{1 + c_\theta|t|^\theta + c_{2\beta}|t|^{2\beta} + c_{1-\alpha}|t|^{1-\alpha} \\ & + \dots \pm I_j|t|^\beta(1 + i_\theta|t|^\theta + \dots) \pm I_l|t|^{\Delta-1} \\ & \pm \dots \pm I_5|t|^{\theta_5} \pm \dots\}, \end{aligned} \quad (3.34)$$

where the coefficients are

$$C^- = 2e_1^2QU^2W_{-2}^0|\tau|^{-\gamma}, \quad c_\theta = U_{4c}W_{-2}^{(4)}|\tau|^\theta/W_{-2}^0, \quad (3.35)$$

$$c_{2\beta} = 6j_2^2(QUW_{-1}^0)^2|\tau|^{2\beta}, \quad I_j = -3j_2QUW_{-1}^0|\tau|^\beta, \quad (3.36)$$

$$i_\theta = U_{4c}[(W_{-1}^{(4)}/W_{-1}^0) + (W_{-2}^{(4)}/W_{-2}^0)], \quad (3.37)$$

$$I_l = \beta e_3W_{-1}^0/e_1UW_{-2}^0, \quad (3.38)$$

$$I_5 = U_{5c}[W_{-2}^{(5)} - 3(W_{-3}^0W_{-0}^{(5)}/W_{-1}^0)]/W_{-2}^0, \quad (3.39)$$

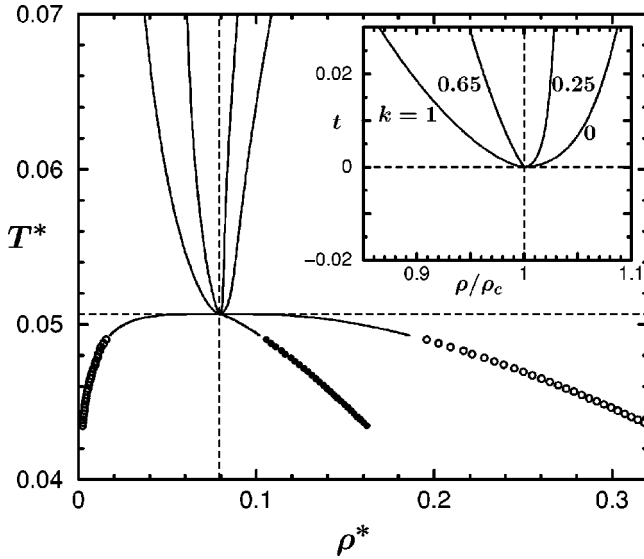


FIG. 2. Plots of coexistence curves, k -susceptibility loci, etc., as in Fig. 1, based on simulations for the restricted primitive model by Luijten *et al.* [25]. The critical parameters adopted are $T_c^* \approx 0.05069$ and $\rho_c^* \approx 0.079$ corresponding to a $\zeta=5$ fine-discretization level [25].

while $c_{1-\alpha}$ has a more complicated form. Now note that the leading asymmetric correction amplitude I_j , given by (3.36), is proportional to j_2 and via (3.23) may also be written simply as

$$I_j = -3j_2B/(1-j_2) \quad (3.40)$$

in terms of the coexistence curve amplitude, B . In order to highlight this feature, it is useful to define a normalized susceptibility difference or *asymmetry factor* by

$$A_\chi(T) \equiv \frac{\check{\chi}_{NN}^+ - \check{\chi}_{NN}^-}{\check{\chi}_{NN}^- + \check{\chi}_{NN}^+}. \quad (3.41)$$

From (3.34), we then obtain

$$\begin{aligned} A_\chi(T) = & I_j|t|^\beta[1 + (i_\theta - c_\theta)|t|^\theta + \dots] + I_l|t|^{\Delta-1} + \dots \\ & + I_5|t|^{\theta_5} + \dots. \end{aligned} \quad (3.42)$$

Evidently, the pressure mixing coefficient j_2 dominates the susceptibility asymmetry near the critical point. This suggests that it may be possible to detect j_2 experimentally by measuring the susceptibilities on the two sides of the coexistence boundary. Note that in case j_2 vanishes, the leading behavior is controlled by $I_l \propto (l_1 + j_1)$ with exponent $\Delta - 1 \approx 0.56_5$ for $d=3$ Ising-type systems.

D. Mixing coefficients

It is clearly of interest to express the linear mixing coefficients entering the scaling fields (1.4)–(1.6) in terms of various thermodynamic quantities which might, at least in principle, be measured in experiments or simulations. As regards the field \tilde{p} , we have already noted in (3.22) the simple expressions for k_0 and l_0 .

The pressure-mixing coefficient, j_2 , can be obtained most simply via (3.16) from the singular amplitudes A_μ in $\mu_\sigma(T)$ and A_p in $p_\sigma(T)$, but it can also be found from the asymmetry in the susceptibilities at coexistence: see (3.39)–(3.41) in Sec. III C. Thus we have

$$j_2 = A_\mu/A_p = -I_j/(3B - I_j), \quad (3.43)$$

where B is the coexistence-curve amplitude defined in (3.20).

Then, from the observable limiting derivatives $\mu'_{\sigma c} \equiv (d\mu_\sigma/dT)_c$ and $p'_{\sigma c} \equiv (dp_\sigma/dT)_c$, which correspond to $\check{\mu}_{\sigma,1}$ and $\check{p}_{\sigma,1}$, we may obtain

$$\begin{aligned} k_1 = & (\rho_c \mu'_{\sigma c} - j_2 p'_{\sigma c})/\rho_c k_B \\ = & [\rho_c \mu'_{\sigma c} - p'_{\sigma c}(A_\mu/A_p)]/\rho_c k_B. \end{aligned} \quad (3.44)$$

The remaining two linear mixing coefficients, j_1 and l_1 , can be obtained by using the amplitudes, $A_{1-\alpha}$ and $S_{1-\alpha}$, in (3.25) and (3.29) which describe the $|t|^{1-\alpha}$ singularity in the density and entropy diameters. Taking a ratio yields

$$\frac{l_1 + j_1}{j_1 k_0 - 1} = \frac{A_{1-\alpha}}{S_{1-\alpha}}, \quad (3.45)$$

where we have used $l_0 = 1$, while k_0 is given in (3.22). On the other hand, from the ratio of $A_{1-\alpha}$ to A_p we obtain via (3.13) and (3.25) the distinct relation

$$\frac{l_1 + j_1}{|\tau|} = \frac{A_{1-\alpha}}{(2-\alpha)(1-j_2)A_p}, \quad (3.46)$$

where τ is given in (3.14). Since τ is linear in the mixing coefficients j_1 and l_1 one can, in principle, solve these two equations for j_1 and l_1 . In practice, however, lack of precision in measuring the amplitudes A_p , $A_{1-\alpha}$, and $S_{1-\alpha}$ is likely to produce large uncertainties.

E. Yang-Yang anomaly

The Yang-Yang relation (1.1) in the two-phase region ($T < T_c$) can be usefully rewritten as [2]

$$C_V(T, \rho) \equiv C_V^{\text{tot}} = (v/v_c) \tilde{C}_p(T) + \tilde{C}_\mu(T), \quad (3.47)$$

where $v = V/N = 1/\rho$ and

$$\begin{aligned} \tilde{C}_p(T) &\equiv v_c T (d^2 p_\sigma / dT^2), \\ \tilde{C}_\mu(T) &\equiv -T (d^2 \mu_\sigma / dT^2). \end{aligned} \quad (3.48)$$

The results (3.11) and (3.15) then yield

$$\begin{aligned} \tilde{C}_p(T) &= \tilde{A}_p |t|^{-\alpha} + \tilde{B}_p + \tilde{a}_p |t|^{\theta-\alpha} + \dots \\ &+ \tilde{b}_1 |t|^{\theta_5 - \alpha - \beta} + \tilde{b}_p |t|^{\theta_5 - \alpha - \beta + \theta} + \dots, \end{aligned} \quad (3.49)$$

$$\begin{aligned} \tilde{C}_\mu(T) &= \tilde{A}_\mu |t|^{-\alpha} + \tilde{B}_\mu + \tilde{a}_\mu |t|^{\theta-\alpha} + \dots \\ &+ \tilde{c}_1 |t|^{\theta_5 - \alpha - \beta} + \tilde{b}_\mu |t|^{\theta_5 - \alpha - \beta - \theta} + \dots, \end{aligned} \quad (3.50)$$

where the various coefficients follow straightforwardly from (3.12)–(3.14), (3.16) and (3.17): see also **K**(3.103). Following Ref. [2] it is reasonable to define the strength of the Yang-Yang anomaly via

$$\mathcal{R}_\mu \equiv \lim_{t \rightarrow 0^-} \frac{\tilde{C}_\mu(T)}{\tilde{C}_p + \tilde{C}_\mu} = \frac{\tilde{A}_\mu}{\tilde{A}_p + \tilde{A}_\mu}. \quad (3.51)$$

By (3.32) this leads immediately to

$$\mathcal{R}_\mu = -j_2 / (1 - j_2). \quad (3.52)$$

Note that \mathcal{R}_μ depends only on j_2 (not on j_1). Fisher and Orkoulas [2] estimated \mathcal{R}_μ for propane from experimental data on the two-phase heat-capacity and obtained $\mathcal{R}_\mu \simeq 0.56$: this suggests $j_2 \simeq -1.27$. They also analyzed the heat capacity data for CO_2 and estimated $\mathcal{R}_\mu \simeq -0.4$ (± 0.3) which implies that j_2 should be positive but small

(less than 1). On the other hand, simulations of the hard-core square-well fluid [6] indicate that \mathcal{R}_μ is small but negative, close to zero: correspondingly, j_2 should be small but positive.

IV. SPECIAL CRITICAL LOCI

In this section we use the scaling formulation to obtain asymptotic expressions for various interesting critical loci that lie in the one-phase regions of the phase diagram. For convenience, we introduce a superscript index ι defined so that: $\iota = \text{i}$ for the locus $\mu = \mu_c$, say, the critical *isokyme*; $\iota = \text{ii}$ for the critical isobar, $p = p_c$; $\iota = \text{iii}$ for the critical isotherm, $T = T_c$; and $\iota = \text{iv}$ for the critical isochore, $\rho = \rho_c$.

A. Critical isokyme, $\mu = \mu_c$

On the critical isokyme $\mu = \mu_c$ (or $\check{\mu} = 0$) the scaling fields (1.4)–(1.6) reduce to

$$\check{p} = \check{p} - k_0 t - m_0 \check{p}^2 - r_0 t^2 - n_3 \check{p} t + \dots, \quad (4.1)$$

$$\check{h} = -j_2 \check{p} - k_1 t - m_2 \check{p}^2 - r_2 t^2 - n_5 \check{p} t + \dots, \quad (4.2)$$

$$\check{t} = t - j_1 \check{p} - m_1 \check{p}^2 - r_1 t^2 - n_4 \check{p} t + \dots. \quad (4.3)$$

Notice that the scaling variable $y = U \check{h} / |\check{t}|^\Delta \sim -(j_2 \check{p} + k_1 t) / |t - j_1 \check{p}|^\Delta$ now diverges, in general, when the critical point is approached (i.e., when $\check{p}, t \rightarrow 0$) since $\Delta > 1$ for fluids. Hence, we need the expansions of the scaling functions $W_\pm^\kappa(y)$ for $y \rightarrow \infty$. On using (2.3), (2.4), and (2.12), we obtain

$$\begin{aligned} \check{p} &= k_0 t + m_0 \check{p}^2 + r_0 t^2 + n_3 \check{p} t + \dots \\ &+ Q W_\infty^0 (U |\check{h}|)^{(2-\alpha)/\Delta} [1 + w_1^0 \check{t} (U |\check{h}|)^{-1/\Delta} + \dots] \\ &+ Q W_\infty^{(4)} U_{4c} (U |\check{h}|)^{(2-\alpha+\theta)/\Delta} [1 + \dots], \\ &+ \tilde{\sigma}_h Q W_\infty^{(5)} U_{5c} (U |\check{h}|)^{(2-\alpha+\theta_5)/\Delta} [1 + \dots], \end{aligned} \quad (4.4)$$

where $\tilde{\sigma}_h = \text{sgn}(\check{h})$. Now \check{t} and \check{h} can be expanded in terms of \check{p} and t using (4.2) and (4.3) and the resulting equation may then be solved iteratively for \check{p} as a function of t . After some algebra, this yields the critical isokyme in the (p, T) plane as

$$\begin{aligned} \check{p}^i(t) &\equiv [p^i(T) - p_c] / \rho_c k_B T_c = \check{p}_1^i t + \check{p}_2^i t^2 \\ &+ A_p^i |t|^{(2-\alpha)/\Delta} [1 \pm b_1^i |t|^{\beta/\Delta} \pm b_2^i |t|^{(\Delta-1)/\Delta} + \dots] \\ &+ b_3^i |t|^{\theta/\Delta} \pm b_4^i |t|^{(\beta+\theta)/\Delta} + \dots + b_5^i |t|^{\theta_5/\Delta} \\ &+ b_6^i |t|^{(\beta+\theta_5)/\Delta} + \dots + \dots, \end{aligned} \quad (4.5)$$

where \pm refers to $t \gtrless 0$ while

$$\check{p}_1^i = k_0, \quad \check{p}_2^i = r_0 + k_0^2 m_0 + k_0 n_3,$$

$$A_p^i = QW_\infty^0(U|k_1 + j_2k_0|)^{(2-\alpha)/\Delta}, \quad (4.6)$$

and the amplitudes b_1^i, \dots of the correction terms are given in **K**(3.111).

Note that the leading singular exponent is $(2-\alpha)/\Delta = 1 + \delta^{-1}$, where $\delta = \Delta/\beta$ is the standard critical exponent characterizing the critical isotherm. In the case of the ($d=3$)-dimensional Ising universality class, $\delta \approx 4.8$ so that $1 + \delta^{-1} \approx 1.21$. This implies that the curvature of $\tilde{p}^i(t)$, the pressure on the critical isokyme, diverges as $T \rightarrow T_c$. Also by convexity—see Sec. II A—the leading singular amplitude A_p^i is positive regardless of the sign of t . On the other hand, it transpires that the amplitude b_5^i of the leading odd correction contains the signum factor $\tilde{\sigma}_h$ so that its sign depends on \tilde{h} . Later we will see that the sign of \tilde{h} can be determined from the mixing coefficient k_1 .

To obtain the critical isokyme in the (ρ, T) plane, we first substitute (4.5) into (4.2) and (4.3) and express \tilde{h} and \tilde{t} as functions of t . Using these results in the definitions (2.15) then yields $\tilde{\rho}$ and \tilde{s} in terms of t . Finally, from (2.18), we obtain the density on the critical isokyme, $\mu = \mu_c$, as

$$\rho^i(T) = \rho_c \{ 1 \pm B^i |t|^{\beta/\Delta} + B_d^i |t|^{2\beta/\Delta} + A_d^i |t|^{(1-\alpha)/\Delta} + \dots \\ \pm B_4^i |t|^{(\beta+\theta)/\Delta} + \dots + B_5^i |t|^{(\beta+\theta_5)/\Delta} + \dots \}, \quad (4.7)$$

where \pm refers to $\tilde{h} \gtrless 0$, while the leading coefficients are

$$B^i = (1 + \delta^{-1})(1 - j_2)A_p^i / |k_1 + j_2k_0|, \\ B_d^i = -j_2(2 - \alpha + \beta)(B^i)^2 / (2 - \alpha)(1 - j_2), \quad (4.8)$$

and the further coefficients are presented in **K**(3.113).

Note that the leading singular exponent is $\beta/\Delta = \delta^{-1}$ which is less than β so implying that the critical isokyme in the (ρ, T) plane is significantly flatter than the coexistence curve. Clearly, therefore, the critical isokyme *below* T_c lies outside the coexistence boundary, i.e., entirely in the one-phase region as is to be expected.

B. Critical isobar

At $p = p_c$ (or $\tilde{p} = 0$), the scaling fields (1.4)–(1.6) with (3.22) reduce to

$$\tilde{p} = -k_0t - \check{\mu} - q_0\check{\mu}^2 - r_0t^2 - v_0\check{\mu}t + \dots, \quad (4.9)$$

$$\tilde{h} = \check{\mu} - k_1t - q_2\check{\mu}^2 - r_2t^2 - v_2\check{\mu}t + \dots, \quad (4.10)$$

$$\tilde{t} = t - l_1\check{\mu} - q_1\check{\mu}^2 - r_1t^2 - v_1\check{\mu}t + \dots. \quad (4.11)$$

As the critical point is approached along a general locus (i.e., $t, \check{\mu} \rightarrow 0$), the scaling variable $y \propto \tilde{h}/|\tilde{t}|^\Delta \sim (\check{\mu} - k_1t)/|t - l_1\check{\mu}|^\Delta$ again diverges. Using the large- y expansion (2.12) for \tilde{p} and rearranging (4.9) yields

$$\check{\mu} = -k_0t - q_0\check{\mu}^2 - r_0t^2 - v_0\check{\mu}t + \dots \\ - QW_\infty^0(U|\tilde{h}|)^{(2-\alpha)/\Delta} [1 + w_1^0\tilde{t}(U|\tilde{h}|)^{-1/\Delta} + \dots] \\ - QW_\infty^{(4)}U_{4c}(U|\tilde{h}|)^{(2-\alpha+\theta)/\Delta} [1 + \dots] \\ - QW_\infty^{(5)}U_{5c}(U|\tilde{h}|)^{(2-\alpha+\theta_5)/\Delta} [1 + \dots]. \quad (4.12)$$

Solving this equation iteratively for $\check{\mu}$ in terms of t with the aid of (4.10) and (4.11) expresses the critical isobar in the (μ, T) plane as

$$\check{\mu}^{ii}(t) = [\mu^{ii}(T) - \mu_c]/k_B T_c = -k_0t + \check{\mu}_2^{ii}t^2 + \dots \\ + A_\mu^{ii}|t|^{(2-\alpha)/\Delta} [1 \pm b_1^{ii}|t|^{\beta/\Delta} \pm b_2^{ii}|t|^{(\Delta-1)/\Delta} + \dots \\ + b_3^{ii}|t|^{\theta/\Delta} \pm b_4^{ii}|t|^{(\beta+\theta)/\Delta} + \dots + b_5^{ii}|t|^{\theta_5/\Delta} \\ + b_6^{ii}|t|^{(\beta+\theta_5)/\Delta} + \dots], \quad (4.13)$$

where \pm again refers to $t \gtrless 0$, while the leading coefficients are

$$\check{\mu}_2^{ii} = -r_0 + k_0v_0 - k_0^2q_0, \\ A_\mu^{ii} = -QW_\infty^0(U|k_1 + k_0|)^{(2-\alpha)/\Delta}, \\ b_1^{ii} = -(2-\alpha)A_\mu^{ii}/\Delta(k_1 + k_0), \quad (4.14)$$

and the further correction amplitudes are given in **K**(3.179).

Note that the curvature of $\check{\mu}^{ii}(t)$ diverges at the critical point with the same exponent as does the critical isokyme in the (p, T) plane: see (4.5). The critical isobar also has the same sign of curvature *above* and *below* T_c in the (μ, T) plane. By thermodynamic convexity, the leading singular amplitude A_μ^{ii} is negative. The amplitude b_5^{ii} of the leading odd correction term again changes its sign depending on \tilde{h} .

In the (ρ, T) plane the critical isobar can be obtained via the same route used above for the critical isokyme. The result is

$$\rho^{ii}(T) = \rho_c \{ 1 \pm B^{ii}|t|^{\beta/\Delta} + B_d^{ii}|t|^{2\beta/\Delta} + A_d^{ii}|t|^{(1-\alpha)/\Delta} + \dots \\ \pm B_4^{ii}|t|^{(\beta+\theta)/\Delta} + \dots + B_5^{ii}|t|^{(\beta+\theta_5)/\Delta} + \dots \}, \quad (4.15)$$

where \pm here refers to $\mu \gtrless \mu_c$ while the leading coefficients are

$$B^{ii} = -(1 + \delta^{-1})(1 - j_2)A_\mu^{ii}/|k_1 + k_0|, \\ B_d^{ii} = -[(2-\alpha)j_2 + \beta](B^{ii})^2/(2-\alpha)(1-j_2), \quad (4.16)$$

where the further coefficients are to be found in **K**(3.121).

Notice that the leading singular behavior matches that of the density on the critical isokyme as given in (4.7). For small $j_2 (< 1)$, the leading amplitude B^{ii} must, by convexity, again be positive. The ratio between B^i in (4.7) and B^{ii} is simply

$$B^i/B^{ii} = |(k_1 + j_2k_0)/(k_1 + k_0)|^{\beta/\Delta}. \quad (4.17)$$

C. Critical isotherm

When $T=T_c$ so that $t=0$, the scaling fields again reduce to yield, now,

$$\tilde{p} = \check{p} - \check{\mu} - m_0 \check{p}^2 - q_0 \check{\mu}^2 - n_0 \check{p} \check{\mu} + \dots, \quad (4.18)$$

and similarly for \tilde{h} and \tilde{t} . Once more, the scaling variable y diverges, in general, on approach to criticality. Using (4.18) and the large- y expansion (2.12) for the scaling functions yields an equation for \check{p} in powers of $\check{\mu}$, \tilde{h} , \tilde{t} , and \check{p} which, as before, can be solved iteratively with the aid of the reduced expansions for \tilde{h} and \tilde{t} to obtain \check{p} as a function of $\check{\mu}$. The result for the pressure on the critical isotherm is

$$\check{p}^{\text{iii}}(\check{\mu}) = [p^{\text{iii}}(\mu) - p_c] / \rho_c k_B T_c = \check{\mu} + \check{p}_2^{\text{iii}} \check{\mu}^2 + \dots + A_p^{\text{iii}} |\check{\mu}|^{(2-\alpha)/\Delta} [1 \pm b_1^{\text{iii}} |\check{\mu}|^{\beta/\Delta} \pm \dots], \quad (4.19)$$

where \pm refers to $\mu \gtrless \mu_c$, while the coefficients are

$$\begin{aligned} \check{p}_2^{\text{iii}} &= m_0 + q_0 + n_0, \\ A_p^{\text{iii}} &= Q W_\infty^0 (U |1 - j_2|)^{(2-\alpha)/\Delta}, \\ b_1^{\text{iii}} &= -j_2 (2 - \alpha) A_p^{\text{iii}} / \Delta (1 - j_2), \end{aligned} \quad (4.20)$$

and the spectrum of higher order terms matches that in (4.13); see also **K**(3.127). The leading singular exponent is again $(2 - \alpha)/\Delta = 1 + \delta^{-1}$, implying that the critical isotherm in the (p, μ) plane has a divergent curvature at the critical point, and thermodynamic convexity ensures $A_p^{\text{iii}} > 0$.

To obtain the critical isotherm in the (ρ, p) plane, we first invert (4.19) to obtain $\check{\mu} \approx \check{p} - A_p^{\text{iii}} |\check{p}|^{(2-\alpha)/\Delta}$ and then use this to express the generalized densities, $\tilde{\rho}$ and \tilde{s} , as functions of \check{p} . Using (2.18) finally yields the critical isotherm in the form

$$\begin{aligned} \rho^{\text{iii}}(p) &= \rho_c \{ 1 \pm B^{\text{iii}} |\check{p}|^{\beta/\Delta} + B_d^{\text{iii}} |\check{p}|^{2\beta/\Delta} + A_d^{\text{iii}} |\check{p}|^{(1-\alpha)/\Delta} + \dots \\ &\quad \pm B_4^{\text{iii}} |\check{p}|^{(\beta+\theta)/\Delta} + \dots + B_5^{\text{iii}} |\check{p}|^{(\beta+\theta_5)/\Delta} + \dots \}, \end{aligned} \quad (4.21)$$

where \pm again refers to $\mu \gtrless \mu_c$ while

$$B^{\text{iii}} = (1 + \delta^{-1}) |(1 - j_1)/(1 - j_2)|^{\beta/\Delta} A_p^{\text{iii}}, \quad (4.22)$$

and $B_d^{\text{iii}} \propto -(B^{\text{iii}})^2$: see **K**(3.131). As expected for the critical isotherm the leading exponent is again $\beta/\Delta = \delta^{-1}$. Assuming that the pressure-mixing coefficient j_2 is small (< 1), we find $B^{\text{iii}} > 0$ owing to convexity. Now when $j_2 = 0$, the scaling field \tilde{h} can be approximated by \check{p} which implies that the critical isotherm in the (ρ, p) plane approaches the critical point from higher density above p_c , while from lower density below p_c : this accords with the observed standard behavior.

D. Critical isochore

Below T_c in normal fluids the critical isochore in the (μ, T) and (p, T) planes coincides with the phase boundary, $\mu_\sigma(T)$ and $p_\sigma(T)$ (but see [23] for exceptions in certain models); however, the behavior above T_c is of general interest. When $\rho = \rho_c$, the result (2.18) for the density leads to

$$\begin{aligned} 0 &= (1 - j_2) Q U |\tilde{t}|^\beta [W_+^{0'}(y) + U_{4c} |\tilde{t}|^\theta W_+^{(4)'}(y) + \dots] \\ &\quad + j_2 (j_2 - 1) Q^2 U^2 |\tilde{t}|^{2\beta} [W_+^{0'}(y) + \dots]^2 + (l_1 + j_1) \\ &\quad \times Q |\tilde{t}|^{1-\alpha} [\Delta y W_+^{0'}(y) - (2 - \alpha) W_+^0(y)] + \dots, \end{aligned} \quad (4.23)$$

where the primes denote differentiation with respect to y . We need to solve this equation for y as a function of \tilde{t} ; but on the critical isochore we expect $y \rightarrow 0$ when $\tilde{t} \rightarrow 0$. Hence we should now use the *small- y* expansions (2.8) for the scaling functions $W_+^0(y)$, $W_+^{(4)}(y)$, etc. The resulting equation in powers of y may be solved iteratively to obtain

$$y = Y_1 |\tilde{t}|^{1-\alpha-\beta} [1 + y_2 |\tilde{t}|^\theta + \dots], \quad (4.24)$$

with coefficients

$$Y_1 = \frac{(2 - \alpha)(l_1 + j_1) W_{+2}^0}{2(1 - j_2) W_{+2}^0 U}, \quad y_2 = -\frac{U_{4c} W_{+2}^{(4)}}{W_{+2}^0}. \quad (4.25)$$

The scaling fields \tilde{p} and \tilde{h} along the critical isochore can now be found as follows: first, on combining (2.3), (2.4) and (2.8) with (4.24), we find

$$\begin{aligned} \tilde{p} &= Q |\tilde{t}|^{(2-\alpha)} [W_{+0}^0 + W_{+2}^0 Y_1^2 |\tilde{t}|^{2-2\alpha-2\beta} + \dots + U_{4c} W_{+0}^{(4)} |\tilde{t}|^\theta \\ &\quad + \dots + U_{5c} W_{+1}^{(5)} Y_1 |\tilde{t}|^{1-\alpha-\beta+\theta_5} + \dots]; \end{aligned} \quad (4.26)$$

then, from the definition (2.1) of the scaling variable y we get

$$\tilde{h} = (Y_1 / U) |\tilde{t}|^{1-\alpha+\gamma} [1 + y_2 |\tilde{t}|^\theta + \dots]; \quad (4.27)$$

finally, by expressing the scaling fields in terms of \check{p} , $\check{\mu}$, and t via (1.4)–(1.6), we can solve these two equations iteratively for \check{p} and $\check{\mu}$ as functions of t . After some algebra, this yields the critical isochore in the (p, T) plane as

$$\begin{aligned} \check{p}^{\text{iv}}(t) &= [p^{\text{iv}}(T) - p_c] / \rho_c k_B T_c = \check{p}_{\sigma,1} t + \check{p}_{\sigma,2} t^2 + \dots \\ &\quad + A_p^{\text{iv}} |t|^{(2-\alpha)} [1 + a_{1p}^{\text{iv}} |t|^\theta + a_{2p}^{\text{iv}} |t|^{\gamma-\alpha} + \dots \\ &\quad + a_{3p}^{\text{iv}} |t|^{1-\alpha-\beta+\theta_5} + \dots] + B_p^{\text{iv}} |t|^{1-\alpha+\gamma} \\ &\quad \times [1 + b_p^{\text{iv}} |t|^\theta + \dots], \end{aligned} \quad (4.28)$$

where the leading amplitudes are

$$A_p^{\text{iv}} = Q W_{+0}^0 |\tau|^{2-\alpha}, \quad B_p^{\text{iv}} = Y_1 |\tau|^{1-\alpha+\gamma} / U, \quad (4.29)$$

while $\check{p}_{\sigma,1}$, $\check{p}_{\sigma,2}$, τ , and the correction amplitudes are given in (3.12), (3.14), and **K**(3.139). The amplitude A_p^{iv} is positive by convexity.

In the (μ, T) plane, the critical isochore is given by the closely analogous form

$$\begin{aligned} \check{\mu}^{\text{iv}}(t) &= [\mu^{\text{iv}}(T) - \mu_c] / k_B T_c \\ &= \check{\mu}_{\sigma,1} t + \check{\mu}_{\sigma,2} t^2 + \dots + j_2 A_p^{\text{iv}} |t|^{2-\alpha} [1 + a_{1p}^{\text{iv}} |t|^\theta \\ &\quad + a_{2p}^{\text{iv}} |t|^{\gamma-\alpha} + \dots + a_{3p}^{\text{iv}} |t|^{1-\alpha-\beta+\theta_5} + \dots] \\ &\quad + (1 + j_2) B_p^{\text{iv}} |t|^{1-\alpha+\gamma} [1 + b_p^{\text{iv}} |t|^\theta + \dots], \end{aligned} \quad (4.30)$$

in which $\check{\mu}_{\sigma,1}$ and $\check{\mu}_{\sigma,2}$ are given in (3.16) and **K**(3.78), while the coefficients A_p^{iv} , a_{1p}^{iv} , etc. are the *same* as in (4.28).

When the pressure-mixing coefficient j_2 vanishes, the leading singular $|t|^{2-\alpha}$ term here vanishes; but in that case the third derivative of $\mu^{\text{iv}}(T)$, the chemical potential on the critical isochore above T_c , diverges at criticality, since one typically has $2 < 1 - \alpha + \gamma < 3$. In view of these results one might also define a magnitude for a Yang-Yang-type of anomaly by comparing the leading singularities in p and μ on the critical isochore *above* T_c ; but this naturally leads to the *identical* ratio! One may thus write $\mathcal{R}_\mu^+ = -j_2 / (1 - j_2) = \mathcal{R}_\mu$: see (3.52).

E. k -susceptibility loci

In this section we focus on the novel k -loci defined in the one-phase region via the isothermal maxima of $\chi^{(k)} \equiv \chi / \rho^k$ in the (ρ, T) plane [6], where $\chi = (\partial \rho / \partial \mu)_T$: see also (2.22). If one considers $\chi^{(k)}$ as a function of μ and T , the maxima of $\chi^{(k)}$ at fixed T satisfy

$$\left(\frac{\partial \chi^{(k)}}{\partial \mu} \right)_T = \frac{1}{\rho^k} \left[\left(\frac{\partial \chi}{\partial \mu} \right)_T - k \frac{\chi}{\rho} \left(\frac{\partial \rho}{\partial \mu} \right)_T \right] = 0. \quad (4.31)$$

This leads to the condition

$$\rho \left(\frac{\partial \chi}{\partial \mu} \right)_T = k \chi^2 \quad \text{or} \quad \check{\rho} \left(\frac{\partial \check{\chi}_{NN}}{\partial \check{\mu}} \right)_T = k (\check{\chi}_{NN})^2; \quad (4.32)$$

see (2.14) and (2.21). By using (2.29), one can obtain the $\check{\mu}$ -derivative of $\check{\chi}_{NN}$ and express the k -locus in terms of the generalized susceptibilities introduced in (2.28). After some algebra, one finds

$$\check{\chi}_{hhh} + (1 + j_2) \check{\rho} \check{\chi}_{hhh} - e_0(k) \check{\chi}_{hh}^2 - 3e_4 \check{\chi}_{hht} + \dots = 0, \quad (4.33)$$

where, by convention, $\check{\chi}_{hhh} \equiv (\partial^3 \check{p} / \partial \check{h}^3)_\check{\tau}$ and $\check{\chi}_{hht} \equiv (\partial^3 \check{p} / \partial \check{h}^2 \partial \check{\tau})$, while

$$e_0(k) = 3j_2 + k(1 - j_2) \quad \text{and} \quad e_4 = (l_1 + j_1) / (1 - j_2). \quad (4.34)$$

The condition may now be converted to scaling form by using (2.3) and (2.4); then by employing the small- y expansions (2.8) one can solve to obtain

$$y \equiv U \check{h} / |\check{\tau}|^\Delta = e_0(k) \check{Y}_1 |\check{\tau}|^\beta + \check{Y}_2 |\check{\tau}|^{1-\alpha-\beta} + \dots, \quad (4.35)$$

which might be compared with (4.24) for the critical isochore. The coefficients are given by

$$\check{Y}_1 = \frac{1}{6} Q U (W_{+2}^0)^2 / W_{+4}^0, \quad \check{Y}_2 = \frac{1}{4} \gamma e_4 W_{+2}^0 / U W_{+4}^0, \quad (4.36)$$

and we may note, for its future significance, that the leading term in (4.35) vanishes identically for the special k value

$$k_{\text{opt}} = -3j_2 / (1 - j_2) = 3\mathcal{R}_\mu. \quad (4.37)$$

At this point the scaling field \check{p} can be expanded in powers of y and $|\check{\tau}|$ via (2.3) and (2.8) and then, via (4.35), wholly in terms of $|\check{\tau}|$. Finally, by using (1.4) and (1.5), and rewriting (4.35) as an expansion for \check{h} one can solve for \check{p} iteratively as a function of t . After some algebra, we find

$$\begin{aligned} \check{p}^{(k)}(t) &= \check{p}_{\sigma,1} t + \check{p}_{\sigma,2} t^2 + \dots + A_p^{(k)} |t|^{2-\alpha} [1 + a_{1p}^{(k)} |t|^\theta \\ &\quad + a_{2p}^{(k)} |t|^{2\beta} + \dots + a_{3p}^{(k)} |t|^{\beta+\theta_5} + \dots] \\ &\quad + B_p^{(k)} |t|^{1+\gamma-\alpha} + \dots, \end{aligned} \quad (4.38)$$

where the leading amplitudes are

$$A_p^{(k)} = Q W_{+0}^0 |\tau|^{2-\alpha} [1 + e_0(k) (W_{+2}^0)^2 / 6 W_{+0}^0 W_{+4}^0], \quad (4.39)$$

$$B_p^{(k)} = \check{Y}_2 |\tau|^{1+\gamma-\alpha} / U, \quad (4.40)$$

while $\check{p}_{\sigma,1}$, $\check{p}_{\sigma,2}$, τ , and the remaining coefficients are given in (3.12), (3.14), and **K**(3.153).

The k -loci in the (μ, T) plane can now be obtained by substituting this result into the scaling fields and using (4.35) once more. The result is

$$\begin{aligned} \check{\mu}^{(k)}(t) &= \check{\mu}_{\sigma,1} t + \check{\mu}_{\sigma,2} t^2 + \dots + A_\mu^{(k)} |t|^{2-\alpha} [1 + a_{1\mu}^{(k)} |t|^\theta \\ &\quad + a_{2\mu}^{(k)} |t|^{2\beta} + \dots + a_{3\mu}^{(k)} |t|^{\beta+\theta_5} + \dots] \\ &\quad + B_\mu^{(k)} |t|^{1+\gamma-\alpha} + \dots, \end{aligned} \quad (4.41)$$

where $\check{\mu}_{\sigma,1}$ and $\check{\mu}_{\sigma,2}$ are given in (3.16) and **K**(3.78) while the principal amplitudes are

$$A_\mu^{(k)} = j_2 A_p^{(k)} + e_0(k) \check{Y}_1 |\tau|^{2-\alpha} / U,$$

$$B_\mu^{(k)} = (1 + j_2) B_p^{(k)}, \quad (4.42)$$

and $a_{i\mu}^{(k)} = j_2 A_p^{(k)} a_{ip}^{(k)} / A_\mu^{(k)}$ for $i = 1, 2, 3$.

For practical purposes the form of the k -loci in the density-temperature plane is of most interest. To that end, note that the generalized densities, $\check{\rho}$ and \check{s} , can be written using the above results as

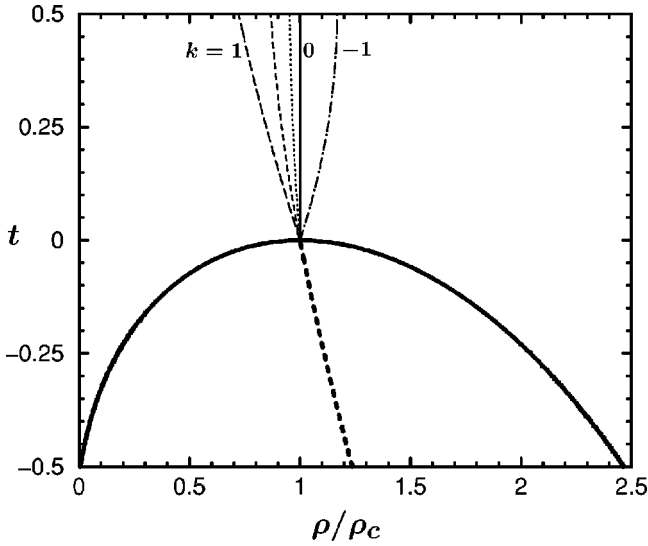


FIG. 3. Selected k -susceptibility loci for the van der Waals equation. The thick solid line represents the coexistence curve while the thick dashed line is the diameter. The ($k=0$) locus is the vertical solid line, while the $k=1, \frac{3}{5}, \frac{1}{4}$ and $k=-1$ loci are portrayed by long-dashed, short-dashed, dotted, and dot-dashed lines, respectively. Note that the $k=\frac{3}{5}$ locus has the same slope at criticality as the coexistence curve diameter.

$$\begin{aligned} \tilde{\rho} = & 2QU[e_0(k)\bar{Y}_1W_{+2}^0|\tilde{t}|^{2\beta} + \bar{Y}_2W_{+2}^0|\tilde{t}|^{1-\alpha} + \dots \\ & + e_0(k)\bar{Y}_1U_{4c}W_{+2}^{(4)}|\tilde{t}|^{2\beta+\theta} + \dots \\ & + \frac{1}{2}U_{5c}W_{+1}^{(5)}|\tilde{t}|^{\beta+\theta_5} + \dots], \end{aligned} \quad (4.43)$$

$$\tilde{s} = Q|\tilde{t}|^{1-\alpha}[(2-\alpha)W_{+0}^0 - \gamma[e_0(k)\bar{Y}_1]^2W_{+2}^0|\tilde{t}|^{2\beta} + \dots], \quad (4.44)$$

where $\tilde{t} \approx \tau t$ with τ defined in (3.14). The k -loci in the (ρ, T) plane are given by

$$\check{\rho}^{(k)}(t) = 1 + (1-j_2)\tilde{\rho} + j_2(j_2-1)\tilde{\rho}^2 - (l_1+j_1)\tilde{s} + \dots, \quad (4.45)$$

so that finally the k -locus varies as

$$\begin{aligned} \rho^{(k)}(T) = & \rho_c \{ 1 + B_d^{(k)}|t|^{2\beta} [1 + b_4|t|^\theta + \dots] + A_d^{(k)}|t|^{1-\alpha} \\ & + A_1^{(k)}t + \dots + B_5^{(k)}|t|^{\beta+\theta_5} + \dots \}, \end{aligned} \quad (4.46)$$

where the coefficients are

$$\begin{aligned} B_d^{(k)} = & 2e_0(k)(1-j_2)\bar{Y}_1QUW_{+2}^0|\tau|^{2\beta}, \\ b_4 = & U_{4c}W_{+2}^{(4)}|\tau|^\theta/W_{+2}^0, \end{aligned} \quad (4.47)$$

$$A_d^{(k)} = -(l_1+j_1)Q|\tau|^{1-\alpha} \left[(2-\alpha)W_{+0}^0 + \frac{1}{2}\gamma(W_{+2}^0)^2/W_{+4}^0 \right],$$

$$(4.48)$$

$$B_5^{(k)} = (1-j_2)QUU_{5c}W_{+1}^{(5)}|\tau|^{\beta+\theta_5}, \quad (4.49)$$

while the expression for $A_1^{(k)}$ is rather complicated. What is significant is that the leading amplitude, $B_d^{(k)}$, varies linearly with k and vanishes identically when k takes the ‘‘optimal value’’ $k_{\text{opt}} = 3\mathcal{R}_\mu$ given in (4.37), while the other coefficients exhibited do *not* vary with k [despite the superscript label (k)]. For $k = k_{\text{opt}}$ we may say, loosely, that the k -locus points most directly to the critical density ρ_c . Indeed, for this reason examining the k -loci may be of value in analyzing both experimental and simulation data. Furthermore the relation to the Yang-Yang anomaly ratio is again revealing and suggestive.

Orkoulas, Fisher and Panagiotopoulos [6] examined the k -loci for the hard-core square-well fluid using grand canonical Monte Carlo simulations. They observed that the k -loci for different system sizes settle down and become independent of size at high enough temperatures. Within the precision attainable these loci can be considered as the true k -loci (for the thermodynamic limit). However, when $T \rightarrow T_c$, the finite-size loci clearly deviate from the limiting behavior. For the data in hand the finite-size effects become evident when $t = (T - T_c)/T_c < 0.1$.

To estimate the k -loci near the critical point, we have fitted the data for $t \geq 0.1$ with the formula (4.46), retaining only the coefficients $B_d^{(k)}$, $A_d^{(k)}$, and $A_1^{(k)}$, while adopting Ising values for the exponents and taking $\rho_c = 0.3067$ and $T_c = 1.2179$ [6]. Some of these estimates are presented in Fig. 1. Similarly, some of the estimated k -susceptibility loci for the restricted primitive model [25] are shown in Fig. 2. For comparison, Fig. 3 presents the k -loci for the van der Waals fluid: see Sec. V. Note that for the van der Waals fluid all the k -loci approach the critical point linearly, which, of course, is consistent with the classical exponent equalities $2\beta = 1 - \alpha = 1$.

F. k -heat-capacity loci

It is also interesting to examine the k -heat-capacity loci or $C_V^{(k)}$ -loci defined by points of maxima of the modified specific heat

$$C_V^{(k)}(T, \rho) \equiv C_V(T, \rho)/\rho^k, \quad (4.50)$$

in the (ρ, T) plane, where C_V is the constant-volume specific heat. These are clearly quite analogous to the k -susceptibility loci discussed in the previous section; but they have not, as yet, been used in any simulations. The $C_V^{(k)}$ -loci can, in principle, be obtained in a way similar to that used for the k -susceptibility loci by starting with the relation (2.27). However, when one takes a derivative of (2.27) with respect to μ at fixed T , the expression becomes complicated and difficult to handle. Therefore we outline a different, canonical approach.

The required maximal points in the (ρ, T) plane at fixed T satisfy

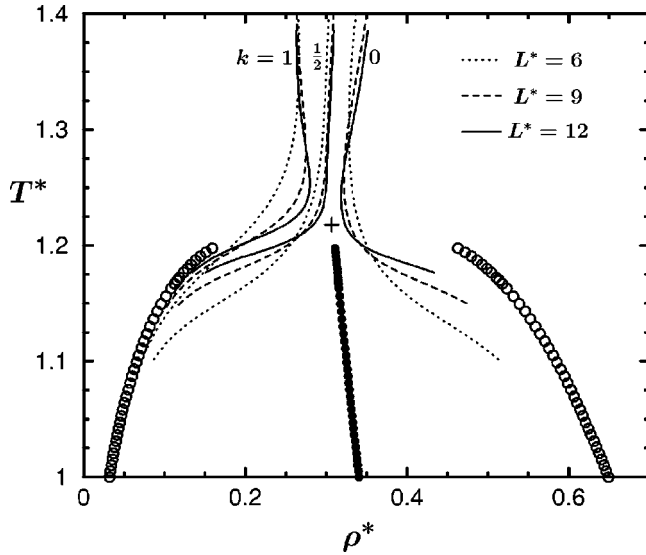


FIG. 4. The k -heat-capacity loci for the hard-core square-well fluid in a finite periodic cube of side L derived from previous simulation data [6]. The dotted curves are the loci for $L^* \equiv L/\sigma = 6$, where σ is the diameter of the hard spheres; the dashed lines are for $L^* = 9$, while the solid lines are for $L^* = 12$. Note that since the systems are finite these loci (and the k -susceptibility loci) extend below T_c .

$$-kC_V + \rho(\partial C_V / \partial \rho)_T = 0. \quad (4.51)$$

To find a convenient expression for $C_V(T, \rho)$, we consider the Helmholtz free energy density $f(\rho, T) = \rho\mu(\rho, T) - p(\rho, T)$. In terms of the reduced variables $\check{\rho}$, $\check{\mu}$ and \check{p} one has

$$\check{f}(\check{\rho}, t) \equiv [f - f_c] / \rho_c k_B T_c = (\mu_c / k_B T_c) \Delta \check{\rho} + \check{\rho} \check{\mu} - \check{p} \quad (4.52)$$

with $\Delta \check{\rho} \equiv \check{\rho} - 1$.

The reduced specific heat, (2.25), is then

$$\check{C}_V(\check{\rho}, t) = (\rho T_c / k_B \rho_c T) C_V = -(\partial^2 \check{f} / \partial t^2)_\rho, \quad (4.53)$$

while the k -locus equation, (4.51), becomes

$$-(k+1)\check{C}_V + \check{\rho}(\partial \check{C}_V / \partial \check{\rho})_t = 0. \quad (4.54)$$

To solve this for $\check{\rho}$ as a function of t , we first expand \check{f} , about the critical density in powers of $\Delta \check{\rho}$ for $t > 0$. If the expansion coefficients are $\check{f}_0(t)$, $\check{f}_1(t)$, \dots , we can rewrite the locus equation as

$$-(k+1)\check{f}_0'' + \check{f}_1'' + [(k-1)\check{f}_1'' + 2\check{f}_2'']\Delta \check{\rho} + O((\Delta \check{\rho})^2) = 0. \quad (4.55)$$

To expand the coefficients $\check{f}_0''(t)$, etc., in powers of t , notice first that, from (4.52) with $\check{\rho} = 1$ or $\Delta \check{\rho} = 0$, we have

$$\check{f}_0(t) = \check{\mu}^{\text{iv}}(t) - \check{p}^{\text{iv}}(t), \quad (4.56)$$

where $\check{\mu}^{\text{iv}}(t)$ and $\check{p}^{\text{iv}}(t)$ represent the variation of μ and p on the critical isochore as obtained in (4.28) and (4.30). Then the relation $\mu(T, \rho) = (\partial f / \partial \rho)_T$ yields

$$\check{f}_1(t) = (\mu_c / k_B T_c) + \check{\mu}^{\text{iv}}(t). \quad (4.57)$$

Finally, we have

$$\check{f}_2(t) = \frac{1}{2} (\partial \check{\mu} / \partial \check{\rho})_t |_{\rho = \rho_c} = \frac{1}{2} \check{\chi}_{NN}^{-1}(t; \rho = \rho_c). \quad (4.58)$$

To obtain the reduced susceptibility, $\check{\chi}_{NN}$, on the critical isochore, we may use (2.29) and the previous results in Sec. IV D. After some algebra we obtain

$$\check{\chi}_{NN} = 2(1 - j_2)^2 Q U^2 W_{+2}^0 |\tau t|^{-\gamma} \times [1 + U_{4c}(W_{+2}^{(4)} / W_{+2}^0) |\tau t|^\theta + \dots], \quad (4.59)$$

where τ was defined in (3.14). Note that the pressure-mixing coefficient j_2 first enters in a $t^{1-\alpha}$ correction; but that is of higher order than the t^θ term retained here. On taking the reciprocal and differentiating twice with respect to t , we finally have

$$2\check{f}_2''(t) = D t^{\gamma-2} [1 - \tilde{d}_\theta t^\theta + \dots], \quad (4.60)$$

where the coefficients are

$$D = \frac{\gamma(\gamma-1) |\tau|^\gamma}{2(1-j_2)^2 Q U^2 W_{+2}^0},$$

$$\tilde{d}_\theta = \frac{(\gamma+\theta)(\gamma+\theta-1) U_{4c} W_{+2}^{(4)}}{\gamma(\gamma-1) W_{+2}^0} |\tau|^\theta. \quad (4.61)$$

We are now in a position to solve (4.55) iteratively for $\Delta \check{\rho}$ as a function of t by using (4.28), (4.30) and (4.60). One finally obtains the k -heat-capacity or $C_V^{(k)}$ -locus in the form

$$\rho_C^{(k)}(T) = \rho_c [1 - B_C^{(k)} t^{2\beta} - A_C^{(k)} t^{2\beta+\alpha} + \dots], \quad (4.62)$$

where, recalling (4.29), (3.12) and **K**(3.68)-(3.78), the amplitudes are

$$B_C^{(k)} = (2-\alpha)(1-\alpha) [1 + k(1-j_2)] A_p^{\text{iv}} / D,$$

$$A_C^{(k)} = [\check{p}_{\sigma,2} + k(\check{p}_{\sigma,2} - \check{\mu}_{\sigma,2})] / D. \quad (4.63)$$

Note first that the exponents 2β and $2\beta+\alpha$ are numerically very close (since $\alpha \approx 0.1$), so the two terms derived compete strongly near the critical point; furthermore, a $|t|^{1-\alpha}$ term also appears in the full expression. However, the leading amplitude $B_C^{(k)}$ does vanish when

$$k = k_C = -1/(1-j_2) = \mathcal{R}_\mu - 1. \quad (4.64)$$

This value can be compared to $3\mathcal{R}_\mu$ for the k -loci: see (4.37). However, one must keep in mind that it will be more difficult

to resolve the “optimal” k value here, compared to the k -susceptibility loci, since the term varying as $t^{2\beta+\alpha}$ does not vanish at $k=k_C$.

In order to gain some impression of the behavior of these $C_V^{(k)}$ -loci, we present in Fig. 4, some of the k -heat-capacity loci obtained for the hard-core square-well fluid in *finite* systems. Note that since the exponents 2β , $2\beta+\alpha$, $1-\alpha$, etc., are closely spaced, it is not feasible to extract reliable estimates of the thermodynamic limiting loci from such finite-size data.

V. CRITICAL LOCI IN CLASSICAL THEORY

In this section, as concrete, albeit rather special, examples of the various critical loci discussed above, we consider the classical theory of a liquid-gas critical point. In particular, the van der Waals equation will be used to provide quantitative illustrations: it reads

$$p = \rho k_B T / (1 - b\rho) - A\rho^2, \quad (5.1)$$

where b and A are constants which measure the molecular size and the strength of the attractive interactions, respectively. As well known, one has

$$k_B T_c = 8A/27b, \quad \rho_c = 1/3b, \quad p_c = A/27b^2. \quad (5.2)$$

Less well known is the behavior when $T \rightarrow 0$ of the liquid and vapor densities and of the phase boundary $\mu_\sigma(T) \rightarrow -A/b$: see **K**(Appendix D).

A. Phase boundaries

The Helmholtz free energy (or its appropriate analog) in a classical or Landau theory may be taken as analytic throughout the critical region. Accordingly, to formulate the theory we expand the free energy density around the critical point in terms of the order parameter

$$m \equiv (\rho - \rho_c) / \rho_c \quad (5.3)$$

and the temperature deviation $t = (T - T_c) / T_c$, as

$$f(T, \rho) = \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} a_{jk} m^j t^k \quad \text{with } a_{20} = a_{30} = 0, \quad (5.4)$$

$$a_{40} > 0,$$

where the conditions stated serve merely to ensure normal critical behavior. The explicit values of the leading coefficients a_{jk} for the van der Waals equation (5.1) are derived in **K**(Appendix C) where it is seen that a special feature is that all the *cubic coefficients*, $a_{3,k}$ ($k=0,1,2,\dots$), *vanish identically*, as do many higher order coefficients such as $a_{j,2}$, $a_{j,3}$, etc., for all $j \geq 2$. Of course, these features should not be expected to hold in real systems or in more realistic models even when a classical description of criticality may be warranted. The leading nonvanishing van der Waals coefficients are reproduced in the Appendix here.

From (5.4), the chemical potential and the pressure can be expanded using

$$\mu(T, \rho) = (\partial f / \partial \rho)_T, \quad p(T, \rho) = \rho \mu - f. \quad (5.5)$$

In the two-phase region, the liquid and vapor phases, with densities $\rho_{\text{liq}} = \rho_c(1 + m_{\text{liq}})$ and $\rho_{\text{vap}} = \rho_c(1 + m_{\text{vap}})$, respectively, must have the same chemical potential, $\mu_\sigma(T)$, and pressure, $p_\sigma(T)$. Solving these two conditions for ρ_{liq} and ρ_{vap} by using (5.3) and (5.4) yields the desired phase boundaries. The detailed calculations are presented in **K** [26]; the results are

$$\bar{m}(T) \equiv \frac{1}{2} (m_{\text{liq}} + m_{\text{vap}}) = \bar{A}_1 t + \bar{A}_2 t^2 + O(t^3), \quad (5.6)$$

$$m_0(T) \equiv \frac{1}{2} (m_{\text{liq}} - m_{\text{vap}}) = B |t|^{1/2} [1 + C_1 t + O(t^2)], \quad (5.7)$$

$$\mu_\sigma(T) = \mu_c + \mu_1 t + \mu_2 t^2 + \mu_3 t^3 + O(t^4), \quad (5.8)$$

$$p_\sigma(T) = p_c + p_1 t + p_2 t^2 + p_3 t^3 + O(t^4), \quad (5.9)$$

where the amplitudes \bar{A}_1 , \bar{A}_2 , B , etc. are expressed in terms of the coefficients a_{jk} in the Appendix. The results agree with those of Sengers and Sengers [13] who, however, give them only to one order lower in t .

B. Critical isochore and analytically continued loci

In addition to examining (i) the *critical isochore* above T_c one may, for critical points describable by classical theory, always consider the *analytical continuation* to $T > T_c$ of various loci otherwise defined only for $T \leq T_c$. Specifically, we will study: (ii) the *continued coexistence curve diameter*, $\bar{\rho}(T)$; (iii) the *continued saturation chemical potential*, $\mu_\sigma(T)$; and (iv) the *continued vapor pressure line*, $p_\sigma(T)$. For nonclassical critical behavior, the analysis of the previous section demonstrates that, in general, these last three continuations cannot be uniquely defined since all carry singularities at T_c .

We address first the appearance of these loci in the (ρ, T) plane: see Fig. 5. The critical isochore, (i), is trivial; the continued diameter, say $\rho_{\text{ii}}(T) [\equiv \bar{\rho}(T)]$, follows directly from (5.7) and has a critical slope

$$(d\rho_{\text{ii}}/dt)_c = \bar{A}_1 \rho_c, \quad (5.10)$$

which is *negative* for the van der Waals equation: see Fig. 5 for which the quadratic terms in t were also computed.

To determine $\rho_{\text{iii}}(T)$, the density locus on which the chemical potential is the analytic continuation of the phase boundary, $\mu_\sigma(T)$, we may substitute (5.8) in the full expansion for $\mu(T, \rho)$ that follows from (5.4) and (5.5). This gives an equation connecting m and t which is easily solved for m in powers of t although the $\mu_2 t^2$ term in (5.8) is needed even in linear order. One finds

$$(d\rho_{\text{iii}}/dt)_c = \rho_c (a_{21} a_{50} - 2a_{31} a_{40}) / 8a_{40}^2. \quad (5.11)$$

The locus $\rho_{\text{iii}}(T)$ can be regarded as an *effective line of symmetry* along which the chemical potential is analytic. However, as seen in Fig. 5, this locus differs from the ana-

lytic continuation of the coexistence curve diameter, $\rho_{ii}(T)$ —another natural candidate—even in the lowest order in t .

The locus $\rho_{iv}(T)$, along which the pressure is the continuation of the vapor pressure curve, $p_\sigma(T)$, can be found in an analogous way. Substituting (5.9) into the expansion of p following from (5.5) leads to

$$(d\rho_{iv}/dt)_c = \rho_c(a_{21}a_{40} + a_{21}a_{50} - 2a_{31}a_{40})/8a_{40}^2, \quad (5.12)$$

which, in fact, differs from both (5.10) and (5.11): see Fig. 5.

In the (μ, T) plane one can find results for the same four loci by using (5.4) and the expressions found for the loci in the (ρ, T) plane. In all cases the initial slopes are the same, that is $(d\mu_\nu/dT)_c = \mu_1$ for $\nu = i - iv$: see Fig. 6. However, the initial curvatures differ, being given by $\rho_c \mu''_{i,c} = 2a_{12}$ and

$$\rho_c \mu''_{ii,c} = 2a_{12} - a_{21}(2a_{31}a_{40} - 2a_{21}a_{50})/2a_{40}^2, \quad (5.13)$$

$$\rho_c \mu''_{iii,c} = 2a_{12} - a_{21}(2a_{31}a_{40} - a_{21}a_{50})/2a_{40}^2, \quad (5.14)$$

$$\rho_c \mu''_{iv,c} = 2a_{12} - a_{21}(2a_{31}a_{40} - a_{21}a_{50} - a_{21}a_{40})/2a_{40}^2, \quad (5.15)$$

where the primes denote differentiation with respect to t . Notice that in Fig. 6 the critical value and a conveniently chosen term linear in t have been subtracted. Thus one can clearly resolve the differences in curvature and observe that the sequence of loci, from top to bottom, is the same as in Fig. 5.

Similarly, the loci in the (p, T) plane can be obtained. Again, all have the same initial slopes while the curvatures are distinct as follows from

$$p''_{i,c} = 2a_{12} - 2a_{02}, \quad (5.16)$$

$$p''_{ii,c} = 2a_{12} - 2a_{02} - a_{21}(2a_{31}a_{40} - 2a_{21}a_{50})/2a_{40}^2, \quad (5.17)$$

$$p''_{iii,c} = 2a_{12} - 2a_{02} - a_{21}(2a_{31}a_{40} - a_{21}a_{50})/2a_{40}^2, \quad (5.18)$$

$$p''_{iv,c} = 2a_{12} - 2a_{02} - a_{21}(2a_{31}a_{40} - a_{21}a_{40} - a_{21}a_{50})/2a_{40}^2. \quad (5.19)$$

In the van der Waals case the curvature $p''_{i,c}$, for the critical isochore, vanishes while $p''_{iv,c}$, for the analytic continuation of $p_\sigma(T)$, is positive so that this locus lies above the critical isochore; the remaining curvatures are all negative and the sequence of loci is again the same as in Fig. 5.

C. k -susceptibility loci

Since the density increases monotonically with μ at fixed T , the maximal condition (4.31) specifying the k -susceptibility loci can be rewritten as

$$\left(\frac{\partial \chi^{(k)}}{\partial \rho}\right)_T = \frac{1}{\rho^k} \left[\left(\frac{\partial \chi}{\partial \rho}\right)_T - k \frac{\chi}{\rho} \right] = 0, \quad (5.20)$$

and, thence, in terms of the free energy density $f(T, \rho)$, in the simpler form

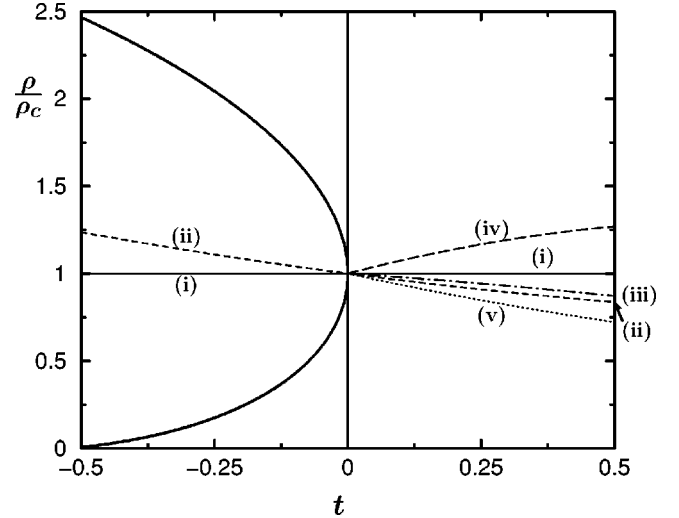


FIG. 5. Various critical loci for the van der Waals equation of state in the (ρ, T) plane, where $m = (\rho - \rho_c)/\rho_c$. The coexistence curve is drawn with a thick solid line. (i) Critical isochore; (ii) coexistence curve diameter and its analytic continuation into the one-phase region; (iii) analytic continuation of $\mu_\sigma(T)$; (iv) analytic continuation of $p_\sigma(T)$; (v) $(k=1)$ -susceptibility locus.

$$k(\partial^2 f / \partial \rho^2)_T + \rho(\partial^3 f / \partial \rho^3)_T = 0. \quad (5.21)$$

Substituting the expansion (5.4) and solving for m iteratively yields the k -loci in the (ρ, T) plane generally as

$$\rho^{(k)}(T) = \rho_c [1 + m_1(k)t + m_2(k)t^2 + O(t^3)], \quad (5.22)$$

with coefficients polynomial in k , namely,

$$m_1(k) = -(ka_{21} + 3a_{31})/12a_{40}, \quad (5.23)$$

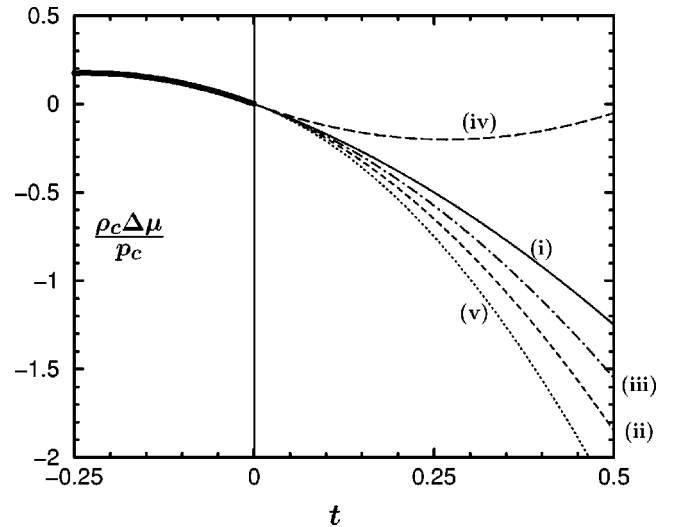


FIG. 6. Critical loci for the van der Waals equation in the (μ, T) plane: $\rho_c \Delta \mu / \rho_c$ is plotted with, for illustrative purposes, $\Delta \mu = \mu - \mu_c - (\mu_1 + \frac{3}{2})t$ [see (A5) and (A13) for μ_c and μ_1]. The graphs include only the second and third order terms in t . The phase boundary, $\mu_\sigma(T)$, is drawn with a thick line. The labeling (i)–(v) is the same as in Fig. 5.

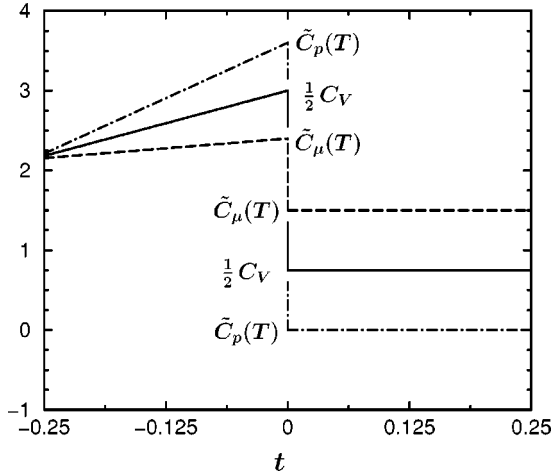


FIG. 7. The specific heat $C_V(T, \rho_c)$ (solid curve) on the critical isochore of a van der Waals fluid (times $\frac{1}{2}$ in units of k_B), compared with the corresponding contributions, $\tilde{C}_p(T)$ and $\tilde{C}_\mu(T)$ (dot-dashed and dashed plots), arising from the isochoric variation of pressure and chemical potential: see (3.48) and (5.26). Note that the standard kinetic contribution to the total specific heat, namely, $\frac{1}{2}dk_B$ (in d dimensions), arises *entirely* from $\tilde{C}_\mu = -T\mu''$. The plots beneath T_c are correct only to leading order in $t = (T - T_c)/T_c$.

$$m_2(k) = -\frac{1}{12} \{ka_{22} + 3a_{32} + 3[(k+1)a_{31} + 4a_{41}]\}m_1(k) + 6[(k+2)a_{40} + 5a_{50}][m_1(k)]^2/a_{40}. \quad (5.24)$$

For the van der Waals equation these results yield

$$m_1(k) = -\frac{2}{3}k, \quad m_2(k) = -\frac{2}{9}k(k^2 + k - 3) \quad (5.25)$$

(see the Appendix). Note that when $k=0$, the coefficients m_1 and m_2 both vanish; furthermore, an exact calculation shows that *all* the expansion coefficients vanish identically at $k=0$ so that one has $\rho^{(0)}(T) \equiv \rho_c$: see Fig. 3. We also find that the slope of the k -locus at criticality becomes equal to that of the coexistence curve diameter when $k = \frac{3}{5}$. In Fig. 3 the k -loci for the van der Waals fluid at several values of k have already been presented. Comparison with Figs. 1 and 2 reveals that the behavior of these loci is closer to those for the hard-core square-well fluid than for the restricted primitive model. Figures 5 and 6 show how the ($k=1$)-susceptibility locus appears in the (ρ, T) and (μ, T) planes and relates to the other van der Waals loci: see the plots labeled v.

D. Yang-Yang relation and some extensions

It is natural to ask how, if at all, a Yang-Yang anomaly might appear in a classical theory. To that end we discuss, in this section, the Yang-Yang relation (1.1) on general linear loci in the (ρ, T) plane and also derive an analogous relation for isotherms.

1. On the critical isochore

On the critical isochore $\rho = \rho_c$, in the two-phase region below T_c , it is convenient here to define the functions

$$C^-(T) \equiv \rho_c T_c^2 \frac{C_V}{T}, \quad \mathcal{P}^-(T) \equiv T_c^2 \frac{d^2 p}{dT^2},$$

$$\mathcal{M}^-(T) \equiv -\rho_c T_c^2 \frac{d^2 \mu}{dT^2}, \quad (5.26)$$

where the factors T_c^2 have been introduced simply for dimensional convenience. [Compare with (3.47)–(3.48).] Above T_c the functions $C^+(T)$, $\mathcal{P}^+(T)$, and $\mathcal{M}^+(T)$ may be defined on the critical isochore in precisely the same way. The Yang-Yang relation then implies $C^\pm = \mathcal{P}^\pm + \mathcal{M}^\pm$. In classical theory we may expand in powers of t for $t \geq 0$ to obtain

$$C^\pm(T) = C_c^\pm + C_1^\pm t + \mathcal{O}(t^2), \quad (5.27)$$

and likewise for $\mathcal{P}^\pm(T)$ and $\mathcal{M}^\pm(T)$. The leading amplitudes above T_c are simply

$$C_c^+ = -2a_{02}, \quad \mathcal{P}_c^+ = 2(a_{12} - a_{02}), \quad \mathcal{M}_c^+ = -2a_{12}, \quad (5.28)$$

while the amplitudes of the terms linear in t are

$$\begin{aligned} C_1^- &= 6(p_3 - \rho_c \mu_3), & C_1^+ &= -6a_{03}, \\ \mathcal{P}_1^- &= 6p_3, & \mathcal{P}_1^+ &= 6(a_{13} - a_{03}), \\ \mathcal{M}_1^- &= -6\rho_c \mu_3, & \mathcal{M}_1^+ &= -6a_{13}, \end{aligned} \quad (5.29)$$

where μ_3 and p_3 are given in the Appendix from which one readily sees that the slopes are discontinuous across T_c .

Indeed, it is well known that the specific heat $C_V(T)$ on the critical isochore exhibits a finite jump at a classical critical point which, in fact, is of magnitude given by

$$\rho_c T_c \Delta C_V = \Delta C \equiv C_c^- - C_c^+ = \frac{1}{2} a_{21}^2 / a_{40}. \quad (5.30)$$

It transpires, however, that in general both the second derivative of the pressure *and* of the chemical potential have a finite discontinuity on the critical isochore. This arises from the presence of the odd coefficients a_{31} and a_{50} (even though a_{31} vanishes “by accident” for the van der Waals equation) as follows from

$$\Delta \mathcal{M} \equiv \mathcal{M}_c^- - \mathcal{M}_c^+ = \frac{1}{2} a_{21} (2a_{31} a_{40} - a_{21} a_{50}) / a_{40}^2, \quad (5.31)$$

with, of course, $\Delta \mathcal{P} = \Delta C - \Delta \mathcal{M}$.

These results are illustrated for a van der Waals fluid in Fig. 7. Clearly, the variation of both the pressure and the chemical potential contribute to the discontinuity in the specific heat on the critical isochore. The relative degree of the two contributions may be gauged by evaluating the ratio

$$\mathcal{R}_\mu \equiv \frac{\Delta \mathcal{M}}{\Delta C} = 2 \frac{a_{31}}{a_{21}} - \frac{a_{50}}{a_{40}}, \quad (5.32)$$

which, as the notation suggests, might be regarded as an effective Yang-Yang ratio for classical systems. Indeed, if \mathcal{R}_μ vanishes, as in the case of simple lattice-gas mean-field models, the isochoric second temperature derivative of the

chemical potential becomes continuous through the critical point: then, the only contribution to the discontinuity in the specific heat on the critical isochore arises from the variation of the *pressure*.

2. On linear density loci

In light of the various critical loci that approach the critical point linearly in the (ρ, T) plane of classical systems (see Fig. 5), it is rather natural to extend the Yang-Yang relation to the general linear locus

$$\rho = \rho_c(1 + rt). \quad (5.33)$$

To that end consider, first, the second temperature derivatives of the pressure and the chemical potential near criticality along this locus. For $T < T_c$, there is no dependence on r because, since the exponent β is less than unity, the linear locus (5.33) always lies in the two-phase region when $T \rightarrow T_c^-$. Hence the results (5.29)–(5.31) still apply. In the single-phase region above T_c , the previous definitions may naturally be extended by taking

$$\mathcal{P}_r^\pm(T) \equiv T_c^2 \left(\frac{\partial^2 p}{\partial T^2} \right)_r, \quad \mathcal{M}_r^\pm(T) \equiv -\rho T_c^2 \left(\frac{\partial^2 \mu}{\partial T^2} \right)_r. \quad (5.34)$$

From (5.4) and (5.5) these functions may be expanded straightforwardly to yield the limiting values

$$\begin{aligned} \mathcal{P}_{r,c}^+ &= 2(2a_{12}r + a_{12} - a_{02}), \\ \mathcal{M}_{r,c}^+ &= -2(a_{12} + 2a_{21}r). \end{aligned} \quad (5.35)$$

In an obvious notation, we then obtain

$$\Delta \mathcal{P}_r = a_{21}(a_{21}a_{40} - 2a_{31}a_{40} + a_{21}a_{50})/2a_{40}^2 - 4a_{21}r, \quad (5.36)$$

$$\Delta \mathcal{M}_r = 4a_{21}r + a_{21}(2a_{31}a_{40} - a_{21}a_{50})/2a_{40}^2. \quad (5.37)$$

When $r=0$, i.e., along the critical isochore, these results of course agree with (5.31).

It is now interesting to define $r_{\mathcal{P}}$ as specifying that locus along which the pressure has a continuous second derivative at criticality and similarly for $r_{\mathcal{M}}$. From (5.36) and (5.37), we thus find

$$r_{\mathcal{M}} = (a_{21}a_{50} - 2a_{31}a_{40})/8a_{40}^2 = r_{\mathcal{P}} - \frac{1}{8} a_{21}/a_{40}. \quad (5.38)$$

For the van der Waals equation these expressions yield $r_{\mathcal{P}} = 0.8$ and $r_{\mathcal{M}} = -0.2$. On the other hand, from (5.10), the locus of the analytically continued coexistence diameter is specified by

$$\bar{r} = (a_{21}a_{50} - a_{31}a_{40})/4a_{40}^2, \quad (5.39)$$

which takes the value $\bar{r} = -0.4$ for the van der Waals equation. Evidently, all three loci are distinct! Note especially, however, that $r_{\mathcal{M}}$ is equal to the slope of the effective line of symmetry at the critical point: see (5.11). Hence, as already shown by Mulholland [28], this putative line of symmetry

for the van der Waals equation differs from the analytic continuation of the coexistence curve diameter; but it is, rather, the locus on which the effective Yang-Yang ratio, $\bar{\mathcal{R}}_\mu$, vanishes!

Now, extending the Yang-Yang relation to the general locus (5.33) leads to

$$\frac{\rho C_V}{T} + \frac{\rho_c^2 r^2}{T_c^2 \rho^2 K_T} = T_c^{-2} [\mathcal{P}_r^\pm(T) + \mathcal{M}_r^\pm(T)], \quad (5.40)$$

where $\rho = \rho_c(1 + rt)$ is understood and, as before, K_T denotes the isothermal compressibility: see **K**(Appendix F).

In classical theory, this relationship may be verified straightforwardly using (5.4), and subsequently derived expressions for $\rho C_V/T$ and $1/\rho^2 K_T$, on (5.33). Explicitly, one finds the initial derivatives of $\mathcal{P}_r^\pm(T)$ and $\mathcal{M}_r^\pm(T)$ at criticality to be cubic polynomials, namely,

$$\mathcal{P}_{r,1}^+ = 6[a_{13} - a_{03} + 2a_{22}r + (a_{21} + 3a_{31})r^2 + 4a_{40}r^3], \quad (5.41)$$

$$\begin{aligned} \mathcal{M}_{r,1}^+ &= -[6a_{131} + 2(a_{12} + 6a_{22})r + (4a_{21} + 18a_{31})r^2 \\ &\quad + 24a_{40}r^3], \end{aligned} \quad (5.42)$$

which, of course, satisfy the generalized relation (5.40) with

$$\rho_c^2/\rho^2 K_T = 2a_{21}t + O(t^2). \quad (5.43)$$

3. Yang-Yang-type relation on the critical isotherm

An important locus in the (ρ, T) plane is the critical isotherm, $T = T_c$. In analogy to the Yang-Yang relation for isochoric variations one can derive a corresponding *isothermal* relation, namely,

$$\frac{1}{\rho^2 K_T} = \left(\frac{\partial^2 p}{\partial \rho^2} \right)_T - \rho \left(\frac{\partial^2 \mu}{\partial \rho^2} \right)_T : \quad (5.44)$$

see **K**(2.97).

To apply this to the critical isotherm, recall that the generally expected critical behavior is

$$1/\rho_c^2 K_T \approx D^\pm |\Delta \rho|^{\delta-1} \quad \text{for } \Delta \rho \equiv \rho - \rho_c \rightarrow 0^\pm. \quad (5.45)$$

In classical theory one has $\delta=3$ and finds $D^+ = D^- = 12a_{40}/\rho_c^4$. More generally one might define the pressure and chemical potential contributions in (5.44) via

$$\begin{aligned} \mathcal{P}_\rho(\rho) &= (\partial^2 p / \partial \rho^2)_T, \quad \mathcal{M}_\rho(\rho) = -(\partial^2 \mu / \partial \rho^2)_T \\ &\quad \text{at } T = T_c. \end{aligned} \quad (5.46)$$

It is then natural to ask, as on the critical isochore, how the two contributions—one from p , and one from μ —contribute to the overall singularity in (5.45) and whether that might throw any further light on the pressure-mixing coefficients j_1 or j_2 . It turns out, however, that matters are very different! In fact, by appropriate integration of (5.45), one can obtain the leading singular behavior of *both* p and μ on the critical isotherm. Then one finds that the lead-

ing singularities of $\mathcal{P}_\rho(\rho)$ and $\mathcal{M}_\rho(\rho)$ both vary as $|\Delta\rho|^{\delta-2}$ and are, thus, *more singular* than is their sum! Indeed, these leading terms must cancel exactly in (5.44) so that the behavior (5.45) for $1/K_T$ appears only as a net correction term. Needless to say, the classical theory fits in with this description although, since δ is an odd integer, there is ambiguity in defining appropriate “singular contributions.” More generally, while there may well be effective ways in which an estimate of the degree of pressure mixing can be found from isothermal observations, we have not identified a good candidate.

VI. SUMMARY

We have carefully formulated a full or “complete scaling theory” for asymmetric fluid criticality that, in particular, incorporates pressure mixing in the basic linear and nonlinear scaling fields. The theory can then describe a Yang-Yang anomaly [2] in which the second temperature derivative of the chemical potential along the phase boundary, namely, $d^2\mu_\sigma/dT^2$, *diverges* at the critical point with the specific heat exponent α . This is shown to entail, also, a leading $|t|^{2\beta}$ term in the coexistence curve diameter that dominates over the previously known $|t|^{1-\alpha}$ term [15] and a dominant $|t|^\beta$ singularity in the normalized susceptibility asymmetry across the coexistence curve. The strength of the Yang-Yang anomaly, \mathcal{R}_μ , is directly related to the linear pressure-mixing coefficient in the ordering field \tilde{h} that we have labeled j_2 .

For convenience of reference, we identify here the main definitions introduced and the explicit results derived. The coefficients $j_1, j_2, k_0, \dots, n_5, v_1, v_2$ entering the *nonlinear scaling fields* to quadratic order are defined via (1.4)–(1.7), in terms of reduced pressure, \check{p} , chemical potential, $\check{\mu}$, and reduced temperature deviation $t = (T - T_c)/T_c$: see (1.7). The *scaling ansatz*, in the form developed is presented in (2.1)–(2.3) and the basic properties of the overall scaling function $W_\pm(y, y_4, y_5, \dots)$ are set out in (2.4) together with (2.8) and (2.10) for small argument, $|y| \rightarrow 0$, and in (2.12) for $|y| \rightarrow \infty$. Explicit expansions in powers of t for the phase boundaries, $p_\sigma(T)$ and $\mu_\sigma(T)$, are reported in (3.11) and (3.15). The corresponding expressions for the *coexistence curve* (and its diameter), and for the entropies of coexisting gas and liquid are (3.20) and (3.21); Eq. (3.31) gives the entropy on the critical isochore, $\rho = \rho_c$, while the susceptibilities on the coexistence curve are presented in (3.34). The linear mixing coefficients themselves are related to measurable critical amplitudes, etc., in (3.22) and (3.43)–(3.46).

Section IV addresses the behavior of various critical loci in the μ, p , and ρ vs T planes. The *critical isokyme*, defined by $\mu = \mu_c$, is described in (4.5) and (4.7); the *critical isobar*, in (4.13) and (4.15); the *isotherm*, in (4.19) and (4.21); and the *critical isochore* in (4.28) and (4.30). The family of *k-susceptibility loci* is defined via (4.31) while (4.38), (4.41) and (4.46), with (4.34) elucidate their behavior in the p, μ , and density vs T planes, respectively: see Figs. 1–3. The analogous *k-heat-capacity loci* are defined in (4.50) while (4.62) describes their appearance in the (ρ, T) plane: see Fig.

4. For both the *k-susceptibility* and *k-heat-capacity loci* there are “optimal” values of k , depending only on the pressure-mixing coefficient j_2 , for which the dominant singularity at criticality vanishes. Thus these particular loci approach the critical point in the (ρ, T) plane almost linearly: see (4.37) and (4.64).

The magnitudes and inter-relations of the various critical loci, including *analytically continued loci*, in the (ρ, T) and (μ, T) planes are illustrated in Figs. 5 and 6, respectively, for the van der Waals fluid. Corresponding analytic results for a general classical fluid, defined via the Landau expansion (5.4), are given in (5.6)–(5.9) and (5.10)–(5.19) and, for the *k-loci*, in (5.22). The Yang-Yang relation and its generalization to a linear density locus [in (5.34) and (5.40)] are discussed for classical systems—for which there is no uniquely defined “anomaly”—in Sec. V D. Figure 7 illustrates that both pressure and chemical potential variation contribute to the specific-heat jump in a van der Waals fluid.

Finally, in part II of this article [29], the present scaling formulation with pressure mixing will be extended to *finite-size systems* (with periodic boundary conditions). The results, which include the definition and analysis of “Q-loci,” are of practical importance in the analysis of simulation data for near-critical asymmetric systems [6,25] as will be further demonstrated [29].

ACKNOWLEDGMENTS

Erik Luijten collaborated in producing the coexistence curve estimates for the restricted primitive model electrolyte presented in Fig. 2. Support from the National Science Foundation (through Grant No. CHE 99-81772) is gratefully acknowledged.

APPENDIX: PHASE BOUNDARIES IN CLASSICAL THEORY

The amplitudes for the coexistence curve introduced in (5.6) and (5.7) are found to be

$$\bar{A}_1 = (a_{21}a_{50} - a_{31}a_{40})/4a_{40}^2, \quad (\text{A1})$$

$$\begin{aligned} \bar{A}_2 = & [a_{31}(4a_{40}^3a_{41} - 4a_{31}a_{40}^2a_{50} + 10a_{21}a_{40}a_{50}^2 - 6a_{21}a_{40}^2a_{60}) \\ & - 4a_{32}a_{40}^4 + a_{50}(4a_{22}a_{40}^3 - 8a_{21}a_{40}^2a_{41} - 6a_{21}^2a_{50}^2 \\ & + 9a_{21}^2a_{40}a_{60}) + 4a_{21}a_{40}^3a_{51} - 3a_{21}^2a_{40}^2a_{70}]/16a_{40}^5, \quad (\text{A2}) \end{aligned}$$

$$B = [a_{21}/2a_{40}]^{1/2}, \quad (\text{A3})$$

$$\begin{aligned} C_1 = & (8a_{22}a_{40}^3 - 8a_{21}a_{40}^2a_{41} + 6a_{21}^2a_{40}a_{60} - 3a_{31}^2a_{40}^2 \\ & + 10a_{21}a_{31}a_{40}a_{50} - 7a_{21}^2a_{50}^2)/16a_{21}a_{40}^3. \quad (\text{A4}) \end{aligned}$$

The coefficients introduced in (5.8) and (5.9) for the phase boundaries, $\mu_\sigma(T)$ and $p_\sigma(T)$, turn out to be

$$\rho_c\mu_c = a_{10}, \quad \rho_c\mu_1 = a_{11}, \quad (\text{A5})$$

$$\rho_c\mu_2 = a_{12} + a_{21}(a_{21}a_{50} - 2a_{31}a_{40})/4a_{40}^2, \quad (\text{A6})$$

$$\begin{aligned} \rho_c \mu_3 = & a_{13} + [a_{31}(a_{31}^2 a_{40}^3 - 4a_{21} a_{31} a_{40}^2 a_{50} - 4a_{40}^4 a_{22} \\ & + 4a_{21} a_{40}^3 a_{41} + 5a_{21}^2 a_{40} a_{50}^2 - 3a_{21}^2 a_{40}^2 a_{60}) \\ & - 4a_{32} a_{21} a_{40}^4 + a_{50}(-4a_{21} a_{22} a_{40}^3 + 4a_{21}^2 a_{40}^2 a_{41} \\ & + 2a_{21}^3 a_{50}^2 - 3a_{21}^3 a_{40} a_{60}) - 2a_{51} a_{21}^2 a_{40}^3 \\ & + a_{70} a_{21}^3 a_{40}^2] / 8a_{40}^5. \end{aligned} \quad (\text{A7})$$

$$p_c = \rho_c \mu_0 - a_{00}, \quad p_1 = \rho_c \mu_1 - a_{01}, \quad (\text{A8})$$

$$p_2 = \rho_c \mu_2 - a_{02} + a_{21}^2 / 4a_{40}, \quad (\text{A9})$$

$$\begin{aligned} p_3 = & \rho_c \mu_3 - a_{03} + a_{21}(4a_{22} a_{40}^3 - 2a_{21} a_{40}^2 a_{41} + a_{21}^2 a_{40} a_{60} \\ & - a_{31}^2 a_{40}^2 + 2a_{21} a_{31} a_{40} a_{50} - a_{21}^2 a_{50}^2) / 8a_{40}^4. \end{aligned} \quad (\text{A10})$$

To specify the corresponding coefficients a_{ij} for the van

der Waals equation [see **K**(Appendix C)] we take Λ_c to be the thermal de Broglie wavelength at $T=T_c$ in a d -dimensional system and define

$$\lambda = \ln(\Lambda_c^d / 2b) - 1. \quad (\text{A11})$$

The leading nonvanishing coefficients are then

$$a_{00} = (\frac{8}{3}\lambda - 3)p_c, \quad a_{01} = a_{00} - p_c, \quad -a_{02} = 3a_{03} = 2p_c, \quad (\text{A12})$$

$$a_{10} = a_{00} + p_c, \quad a_{11} = \frac{8}{3}\lambda p_c, \quad -a_{12} = 3a_{13} = 2p_c, \quad (\text{A13})$$

$$a_{20} = 0, \quad a_{21} = 3p_c, \quad a_{40} = a_{41} = \frac{3}{8}p_c, \quad (\text{A14})$$

$$a_{50} = -\frac{3}{40}p_c, \quad a_{60} = \frac{9}{80}p_c, \quad a_{70} = -\frac{3}{56}p_c. \quad (\text{A15})$$

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