

Scaling laws for fluid systems using generalized homogeneous functions of strong and weak variables*

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We present a systematic approach to scaling at ordinary critical points with special emphasis on the critical point of a single-component fluid. Recent work on scaling in fluids has avoided the possibility of a singular coexistence surface. In particular, the consequences of satisfying the inequality $\theta \leq \alpha + \beta$ as an equality have not been explored. We show that $\theta = \alpha + \beta$ is a prediction of scaling, and that, if $\theta = \alpha + \beta$, the specific heat at constant volume has a leading-order (α -divergent) asymmetry across the coexistence surface. We further show that the asymmetric nature of the fluid critical point precludes the analyticity of the critical isochore above the critical temperature, whether the critical isochore is expressed in terms of $\mu(T)$ or $P(T)$. A weak singularity of the form $|T - T_c|^{\beta - 2(\alpha + \beta)}$ is predicted for the isochore, which may be dominated by stronger singularities.

I. INTRODUCTION

The original scaling hypothesis was made by Widom¹ (and, independently, by others²) to describe behavior near the critical point of a fluid. More recently, it has been realized that this form of the scaling hypothesis may only be adequate to describe the *leading-order* behavior of models and real fluid systems. The interest in extending the domain of validity of the scaling hypothesis has been stimulated by the discovery of a singular diameter³ in certain models^{4,5} and by recent renormalization-group calculations⁶; the singularity behaves like $|T - T_c|^{1-\alpha}$, where α ($\alpha > 0$) is the exponent characterizing the divergence of the specific heat, C_V . Mermin and Rehr⁷ have suggested that this $(1 - \alpha)$ singularity may be expected generally in fluids.

To incorporate the diameter singularity, Cook and Green⁸ have suggested a very general equation of state. It contains as its leading term the scaling equation of state and many less singular terms. These corrections to scaling yield the diameter singularity and other weakly singular corrections to leading-order scaling behavior. On the other hand, Rehr and Mermin⁹ have shown that the singular diameter can be derived from a simple modification of the original scaling equation.

In 1965, Griffiths¹⁰ derived the rigorous inequality $\theta \leq \alpha + \beta$, where θ is the exponent characterizing the divergence of the curvature of the vapor pressure curve, $(\partial^2 P / \partial T^2)_V$. In Refs. 8 and 9 this Griffiths inequality is not satisfied as an equality since assumptions are made about the smoothness of the chemical potential (Ref. 9) or the degree of symmetry about the liquid-vapor coexistence surface. This suggests that the approaches of Refs. 8 and 9 do not explore the con-

sequences of the scaling hypothesis for fluids in the most general way.

In this work, we show how to formulate a scaling hypothesis which can satisfy the Griffiths inequality $\theta \leq \alpha + \beta$ as an equality. To separate physical assumptions from mathematical assumptions, we consider the general problem of making a scaling hypothesis at an ordinary critical point with special attention paid to the liquid-vapor critical point. To make a scaling hypothesis for a fluid system the following four decisions must be made: (i) which thermodynamic variable to select as the dependent variable of the scaling equation; (ii) what independent variables to choose in the scaling equation; (iii) what curves in the thermodynamic space to describe and how to express them in the variables chosen; (iv) whether to augment the scaling equation with correction terms. We will illustrate these four decisions by examining the assumptions implicit in the original scaling hypothesis proposed by Widom¹:

(i) First, a particular thermodynamic potential must be selected as a candidate for a scaling equation. For fluids, Widom chooses the pressure, P . Each choice of a potential carries with it a natural set of variables (here μ and T , where μ is the chemical potential and T the temperature) and a natural set of associated thermodynamic quantities given by the partial derivatives of the potential with respect to these natural variables. For example, the number density ρ is given by $\rho = (\partial P / \partial \mu)_T$. On the other hand, if one chooses the Gibbs potential, $G(P, T)$, then the volume V is given by $V = (\partial G / \partial P)_T$. [For a magnetic system, $-M = (\partial G / \partial H)_T$, where M is the magnetization and H is the magnetic field.] Symmetries or asymmetries in quantities such as ρ or V , will differ depending on the choice of variables and potential (cf. Fig. 1).

(ii) Second, one must choose variables in which to state the scaling equation. Widom chooses $\mu - \mu(T)$ and T , where $\mu(T)$ describes the coexistence surface for $T < T_c$, and the critical isochore for $T > T_c$. The choice of T as the second variable instead of some combination of μ and T , coupled with Widom's use of a single scaling function, has the consequence that the density diameter is rectilinear (cf. Sec. III). The $|T - T_c|^{1-\alpha}$ dependence of the diameter can be obtained in two ways (a) by allowing the second variable to be a function of μ and T , and (b) by adding correction terms to the scaling equation. As we will see in Sec. III, the amplitude of the $|T - T_c|^{1-\alpha}$ term in the diameter is explicitly related to the amplitudes of leading order singularities in case (a), while in case (b) the amplitudes need have no relationship. Thus, the use of a different "second variable" (instead of T), which Rehr and Mermin⁹ call "revised scaling," gives the expected form of the diameter singularity but may not correctly give the associated amplitude, as they have pointed out.

(iii) Third, one must decide which surfaces in the thermodynamic space to describe and how to describe them in terms of the scaling variables. By his choice of $\mu - \mu(T)$ as his first variable, Widom singles out the liquid-gas coexistence surface (i.e., the vapor pressure curve) and the critical isochore and describes them both by the homogeneous¹¹ equation $\mu - \mu(T) = 0$. The coexistence surface is a natural choice in that it is the real phase boundary. The critical isochore is not a natural choice in this sense, but both the coexistence surface critical isochore correspond to paths utilized in experimental measurements, making it highly desirable to describe these paths. The use, however, of a homogeneous¹¹ description of these paths by an equation $x_1 = 0$, where x_1 is some appropriate variable, limits the scaling approach to systems described by smooth¹² surfaces. To see this statement, suppose that $\mu(T)$ were singular on the coexistence surface or critical isochore. Then the variable $x_1 = \mu - \mu(T)$ would have singularities at $T = T_c$ even away from the critical point. This behavior is undesirable although perhaps tolerable if the singularity were sufficiently weak.¹³ Since the singularity in the vapor pressure $P(T)$ [and its critical isochore continuation for $T > T_c$] is expected to be strong, having a divergent curvature, $(\partial^2 P / \partial T^2)_v \rightarrow \infty$ as $T \rightarrow T_c$, there has been a nearly universal avoidance of $p-t$ scaling of G . (Here we utilize the reduced variables, $p \equiv P - P_c$ and $t \equiv T - T_c$.) In this work we weaken Widom's assumption to allow inhomogeneous¹¹ descriptions of the critical isochore and coexistence surface in order to en-

compass the more general situation. This permits us to consider $p-t$ scaling of the Gibbs potential G as well as $\mu-t$ scaling of the pressure P .

(iv) Fourth, one must decide whether to describe the system with a single scaling function or to augment the scaling equation with correction terms. Widom's choice of a single function accounts for the leading-order singular behavior and, as extended in Ref. 9, places strong restrictions on the forms and amplitudes of asymmetries and other weakly divergent corrections to the leading-order behavior. On the other hand, multiple correction terms give considerable freedom to the equation of state. Therefore, it is possible that the revised scaling approach of Rehr and Mermin⁹ gives only the qualitative nature of the diameter, but cannot correctly predict the amplitude.

In Sec. IIA we introduce a general potential Ψ which could be taken to be (within a linear term subtracted off) either $P(\mu, T)$ or $G(P, T)$ for fluids [or, for the sake of comparison, $G(H, T)$ for a magnetic system]. We initially choose to describe the system with a single scaling function to simplify the exposition and to explore the limitations of this approach.

In Sec. IIB we discuss the restrictions that can be placed on the forms of the scaling variables used to describe the system. We show that the preferred ("weak") direction of Griffiths and Wheeler,¹⁴ as reflected in the scaling variables, is an automatic consequence of the scaling hypothesis. That is, one of the scaling variables, x_1 , must be chosen such that the line $x_1 = 0$, the x_2 axis, is tangent to the coexistence surface at the critical point. We further show that a change in the second variable, x_2 , generates a series of correction terms to the scaling equation of a form suggested by a restriction of the formalism of Cook and Green.⁸

In Sec. IIC we form a hypothesis for the description of the coexistence surface and critical isochore in terms of the scaling variables x_1 and x_2 . The scaling-invariant form $x_1 = Ax_2^{\beta\delta}$ is suggested by the scaling hypothesis. We show that this choice in a fluid system corresponds to a vapor-pressure curve with a divergent curvature, $(\partial^2 P / \partial T^2)_v$, characterized by an exponent $\theta = \alpha + \beta$, and an asymmetry in the amplitudes of the specific-heat divergence across the coexistence surface (cf. Sec. III).

In Sec. III we derive the usual critical-point exponents and the relationships between the amplitudes of the leading-term singularities and those of the asymmetries, such as the diameter, utilizing the scaling-invariant parametric form $x_1 = Ax_2^{\beta\delta}$ for the coexistence surface and critical

isochore. We then show that if a single scaling function is used, this scaling-invariant form cannot suffice on the critical isochore, but it must be modified by the addition of a specific correction term.

II. A MODIFIED SCALING HYPOTHESIS AT AN ORDINARY CRITICAL POINT

A. Choice of potential and scaling equation

We consider a system that can adequately be described near its critical point by a potential Ψ which can be expected to scale. By keeping Ψ general, we can discuss p - t and μ - t scaling in fluids and H - t scaling in a simple magnetic system, simultaneously. For example, in a magnetic system, we can choose $\Psi = G(H, T) - G_c + S_c(T - T_c)$,¹⁵ where S is the entropy (the subscript c denotes the value at the critical point).

For simplicity we choose to describe Ψ with one scaling function and we employ initially arbitrary scaling variables. In the simple case of a single function, we write

$$\Psi = \mathcal{S} + \mathcal{B}, \quad (2.1)$$

where the scaling function $\mathcal{S}(x_1, x_2)$ is a generalized homogeneous function (GHF)

$$\lambda \mathcal{S}(x_1, x_2) = \mathcal{S}(\lambda^{a_1} x_1, \lambda^{a_2} x_2), \quad (2.2)$$

and $\mathcal{B}(x_1, x_2)$ is a C^∞ background term which vanishes and whose first partial derivatives vanish at the critical point $(0, 0)$. We choose x_1 and x_2 to be smooth invertible functions of the usual thermodynamic variables, y_1 and y_2 . For example, in the simplest Ising ferromagnet, $x_1 = y_1 = H$ and $x_2 = y_2 = t$. The convention $a_1 > a_2$ labels x_1 and x_2 as the strong and weak variables of Griffiths and Wheeler.^{14, 16} By restricting the transformation to be smooth and invertible, we exclude those

cases in which the geometry of the transformation may be as important or more important than that of the scaling function \mathcal{S} . In particular, the parametric representations of Schofield¹⁷ embody the singularities directly into the transformed variables used in the parametrization. The transformation is singular and noninvertible at the critical point.

Of the large number of thermodynamic quantities, we will discuss in detail three: C , which is an "order parameter" for the system; D_s , a typical strongly divergent quantity; and D_w , a typical weakly divergent quantity.¹⁴ In terms of the potential Ψ , these are given by

$$C \equiv \Psi^1, \quad (2.3)$$

$$D_s \equiv \Psi^{11}, \quad (2.4)$$

$$D_w \equiv (\Psi^{11}\Psi^{22} - \Psi^{12}\Psi^{12})/\Psi^{11}; \quad (2.5)$$

we introduce the notation

$$F^i \equiv \frac{\partial F}{\partial y_i}; \quad F_i \equiv \frac{\partial F}{\partial x_i}. \quad (2.6)$$

Table I lists the specific symbols for Ψ , C , D_s , y_1 , y_2 , and D_w , for the three cases considered in this work.

B. Restrictions on the forms of the variables x_1 and x_2

It is straightforward to show¹⁸ that the scaling hypothesis (2.2) implies that near the critical point

$$\frac{\partial^2}{\partial y_1^2} \rightarrow - \left(\frac{\partial y_1}{\partial y_2} \right)_c, \quad (2.7)$$

where we use the notation

TABLE I. Values of symbols used in the text in three cases. Symbols not defined in the text are $s \equiv S/V$ (entropy density) and K_T , the isothermal compressibility.

	μ - t scaling	p - t scaling	Magnetic system
Ψ	$P - P_c - \rho_c(\mu - \mu_c) - (T - T_c)s_c$	$G - G_c + (T - T_c)S_c - (P - P_c)V_c$	$G - G_c + (T - T_c)S_c$
y_1	$\mu - \mu_c$	$p \equiv P - P_c$	H
y_2	$t \equiv T - T_c$	$t \equiv T - T_c$	$t \equiv T - T_c$
C	$\rho - \rho_c$	$v \equiv V - V_c$	$-M$
D_s	$\rho^2 K_T$	$\left(\frac{\partial V}{\partial P} \right)_T$	$-\chi_T - \left(\frac{\partial M}{\partial H} \right)_T$
D_w	$\rho C_V / T$	$-C_V / T$	$-C_M / T$
$\left(\frac{\partial y_1}{\partial y_2} \right)_c$	$\left(\frac{\partial \mu}{\partial T} \right)_\rho$	$\left(\frac{\partial P}{\partial T} \right)_V$	$\left(\frac{\partial H}{\partial T} \right)_M$

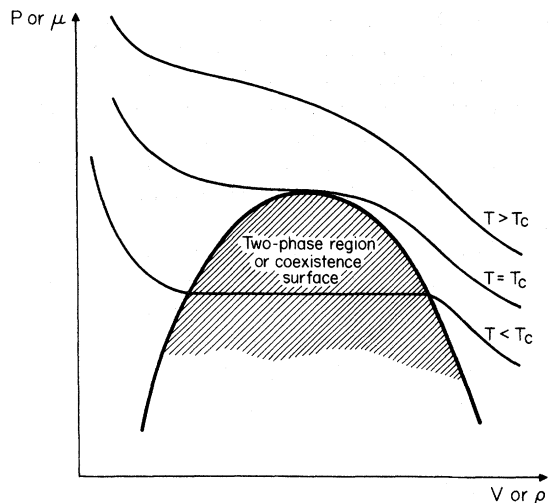


FIG. 1. View of the coexistence surface in $P - V$ or $\mu - \rho$ plane for the case of an asymptotically symmetric top.

$$b_j^i \equiv \frac{\partial x_i}{\partial y_j} \tag{2.8}$$

Equation (2.7) is proved under less restrictive hypotheses (than the scaling hypothesis) in Ref. 18. Equation (2.7) shows that the line $x_1 = 0$, which is the x_2 axis, must be tangent to the critical isochore at the critical point, as postulated in Ref. 14 (cf. Fig. 2). We assume that the derivative (2.7) is continuous from above T_c to below T_c so that the x_2 axis is also tangent to the coexistence surface at the critical point. Equation (2.7) determines x_1 to linear order. In general, x_1 will have higher-order dependence on y_1 and y_2 ; however, this dependence cannot be extracted from leading-term or even first-nonleading-term behavior of any thermodynamic quantity. The linear dependence of x_2 must be determined from nonleading-

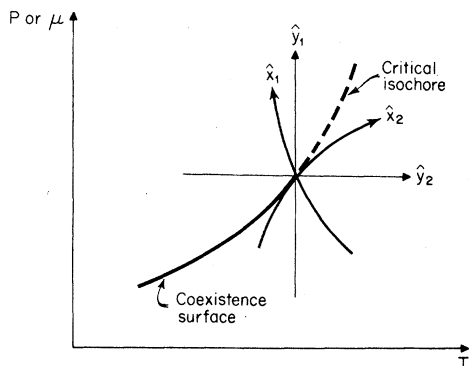


FIG. 2. Relationship between the x_2 axis and the coexistence surface. The dashed line denotes the critical isochore for $T > T_c$.

order terms, so that the higher-order dependence of x_2 is even more difficult to extract. For this reason, we will discard any term which does not dominate these weak singularities coming from the nonlinear portions of the transformation between (x_1, x_2) and (y_1, y_2) .

The original postulate of Griffiths and Wheeler¹⁴ (that the strong direction, the x_1 axis, is arbitrary), however, is correct if and only if we consider solely leading terms in the expressions for thermodynamic quantities. Our scaling hypothesis (2.1) is stated in terms of a GHF, \mathcal{S} ; for a function which is a GHF to remain a GHF after a change of variables, the change of variables is severely limited. The transformation cannot be linear in both variables unless either it is the unit transformation or the scaling powers are equal. The proof of these statements is given in Appendix A.

If we consider a linear transformation in one variable, setting $X_2 = x_2 - (\text{const})x_1$, our GHF, $\mathcal{S}(x_1, x_2)$, can be expanded as a sum of GHF's:

$$\mathcal{S}(x_1, x_2) = \mathcal{S}(x_1, X_2) + (\text{const})x_1 \mathcal{S}_2(x_1, X_2) + [(\text{const})^2/2!] x_1^2 \mathcal{S}_{22}(x_1, X_2) + \dots \tag{2.9}$$

Equation (2.9) is a series of correction terms of the form suggested⁸ to account for certain of the asymmetries in a fluid. For example, one can easily show that the second term on the right-hand side of (2.9) can be written

$$|X_2|^{(1-a_2+a_1)/a_2} Q \left(\frac{x_1}{|X_2|^{a_1/a_2}} \right) = |X_2|^{2-\alpha+\beta\delta-1} Q \left(\frac{x_1}{|X_2|^{\beta\delta}} \right) \tag{2.10}$$

For the convenience of the reader, the right-hand side of (2.10) utilizes the expressions in terms of a_1 and a_2 of the critical-point exponents to be obtained in Sec. III.

If we try a more general smooth change of variables, we generate a more general series of corrections. However, the most singular of these corrections will still be given by the linear part of the change of variables. *It is important to observe that a linear change in the strong variable x_1 generates a series of correction terms, each of which is more singular than the previous terms.* Therefore, even if we did not have (2.7) we would not be free to choose x_1 arbitrarily. This statement is a special case of the situation for n variables discussed in Appendix A.

The correction terms of (2.9) are explicitly related to the original GHF, \mathcal{S} . They are not, of course, the most general correction terms of the same form. However, if for some choice of x_2 the corrections of the form (2.10) vanished identical-

ly, then revised scaling⁹ alone would be sufficient to account for all the asymmetries discussed (at least to leading order in those asymmetries). On the other hand, one may be forced to include correction terms from the beginning. In this case, a change of x_2 simply changes the exact form of the correction terms without changing their qualitative nature; x_2 can be chosen "arbitrarily." The use of revised scaling relates the amplitudes of the weaker singularities to those of the stronger singularities, and is therefore capable of sharper testing when compared to models or experiment, than the corrections-to-scaling approach⁸ which leaves the weak amplitudes independent of the leading-term amplitudes. If revised scaling⁹ does correctly give the weak amplitudes, then the x_1 axis forms a second preferred direction in the sense that it defines the most appropriate variables in which to state the scaling equation.

The x_2 variable, although unspecified, has a simple form on many paths. It is essentially equal to y_2 . To see this, observe that on any path Γ ,

$$\left(\frac{dx_2}{dy_2}\right)_\Gamma = \frac{J}{b_1^1 - b_1^2(dx_1/dx_2)_\Gamma}, \quad (2.11)$$

where J denotes the Jacobian of the transformation between (x_1, x_2) and (y_1, y_2) ,

$$J = b_1^1 b_2^2 - b_2^1 b_1^2. \quad (2.12)$$

We assume that J is nearly constant near the critical point; this is consistent with our assumption of a C^∞ transformation. For convenience we will normalize our variables so that at the critical point $J = 1$ and $b_1^1 = 1$.

In this case, an approximate integral of (2.12) is

$$x_2 = y_2 + b_1^2 x_1(x_2). \quad (2.13)$$

We will see that on the coexistence surface and critical isochore $dx_1/dx_2 \rightarrow 0$ at the critical point, so that the approximation in (2.13) is a good one.

C. Forms of the coexistence surface and critical isochore

We choose to describe the critical isochore as well as the coexistence surface, since experiments are performed along both paths; as we will show in Sec. III, the critical-isochore path is slightly inconvenient theoretically.

On all paths passing through the critical point, the singularities of Ψ in (2.1) are assumed to come from terms involving \mathcal{S} . We know from (2.7) that $x_1 \approx 0$ on both the critical isochore and coexistence surface. Using the properties of GHF's we write

for \mathcal{S}_i and \mathcal{S}_{ij} :

$$\mathcal{S}_i(x_1, x_2) = |x_2|^{(1-a_i)/a_2} \mathcal{S}_i(x_1/|x_2|^{a_1/a_2}, \pm 1), \quad (2.14a)$$

$$\mathcal{S}_{ij}(x_1, x_2) = |x_2|^{(1-a_i-a_j)/a_2} \mathcal{S}_{ij}(x_1/|x_2|^{a_1/a_2}, \pm 1). \quad (2.14b)$$

The upper sign is used for x_2 positive and the lower sign for x_2 negative.

Equations (2.14) suggest the possible validity of the following scaling-invariant form for the relationship between the scaling variables on paths of interest:

$$x_1 = A_\pm |x_2|^{a_1/a_2} = A_\pm |x_2|^{\beta\delta}. \quad (2.15)$$

In (2.15), A_\pm is a constant, possibly zero, which may differ above and below T_c (the subscript denotes the sign of $T - T_c$).

The limiting case, $A_\pm = 0$, reduces to the homogeneous relation $x_1 = 0$, corresponding to a smooth form for the phase boundary and critical isochore. The case of $A_\pm \neq 0$ gives a power-law singularity. We observe that on any path Γ ,

$$\left(\frac{dy_1}{dy_2}\right)_\Gamma = -b_2^1 + \left(\frac{dx_1}{dx_2}\right)_\Gamma \left(\frac{dx_2}{dy_2}\right)_\Gamma. \quad (2.16)$$

The b_j^i are smooth by assumption and by (2.13), $(dx_2/dy_2)_\Gamma$ is nearly constant. We therefore expect that the curvature of the path d^2y_1/dy_2^2 on a scaling-invariant path (2.15) will be given approximately by

$$\left(\frac{d^2y_1}{dy_2^2}\right)_\Gamma \sim \left(\frac{d^2x_1}{dx_2^2}\right)_\Gamma \sim |y_2|^{(a_1-2a_2)/a_2} \sim |y_2|^{-\theta}, \quad (2.17)$$

where the exponent is given by

$$\theta = \alpha + \beta. \quad (2.18)$$

In both p - t and μ - t scaling, (2.18) satisfies the inequality¹⁰ $\theta \leq \alpha + \beta$ as an equality.^{19(a)} Physical necessity (as well as convenience) suggests the relationship (2.15) for the coexistence surface. In the two-phase region below T_c , there are two branches of \mathcal{S} corresponding to the liquid and gas phases. The coexistence surface is defined by the equality of \mathcal{S} on these two branches; that is, on the coexistence surface,

$$\mathcal{S}^{\text{liquid}}(x_1, x_2) = \mathcal{S}^{\text{gas}}(x_1, x_2). \quad (2.19)$$

Only the form given in (2.15) allows (2.19) to be satisfied exactly,^{19(b)} if a single scaling function is used. On the other hand, we will show in Sec. III that if a single scaling function is used, (2.15) cannot be used on the critical isochore and must

be modified by the addition of corrections.

Before we present the detailed results of our modified scaling hypothesis, a discussion of the use of any inhomogeneous description is in order.¹¹ In the p - t scaling case, for example, we can write the form of the coexistence surface as

$$p - (\text{const})t - (\text{const}')t^2 + \dots = A_- |t|^{2-\theta} + \dots \quad (2.20)$$

The left-hand side of (2.20) is an acceptable choice for x_1 ; that is, it satisfies (2.7). Using (2.13) we could rewrite (2.20) to lowest order as

$$x_1 = A_- |x_2|^{2-\theta}. \quad (2.21)$$

(A similar situation might exist in μ - t scaling with the possibility that $\theta < 0$.) We assume, therefore, that any nonanalyticity on the coexistence surface or critical isochore can be expressed in an inhomogeneous way such as (2.15) or (2.21). This is equivalent to defining x_1 to be some or all of the smooth part of the coexistence surface and critical isochore. If both of these are smooth, we have the case treated by Widom. If one is smooth, but the other is not, x_1 is the analytic continuation of the smooth surface.

III. RESULTS OF REVISED SCALING

In this section we develop the results of a revised-scaling hypothesis using a single scaling function with no correction terms [cf. Eq. (2.1)] and utilizing the scaling invariant form (2.15) to describe the coexistence surface and critical isochore. We derive the usual critical-point exponents and relate the amplitudes of the weaker singularities to the amplitudes of the dominant singularities in C , D_s , and D_w . We show that the use of (2.15) with A_\pm nonzero changes both the leading and nonleading amplitudes and gives a leading-term (α -divergent) liquid-gas asymmetry in D_w across the coexistence surface. Finally, we show that the use of a single scaling function and the scaling-invariant form are incompatible on the critical isochore; to retain a single scaling function, Eq. (2.15) must be modified. This modification has the consequence that a weak singularity is predicted for the pressure of a fluid system on the isochore similar to one found in the corrections-to-scaling approach of Cook and Green.⁸

Employing Eq. (2.15), and utilizing the properties of GHF's, we can express the quantities Ψ , C , D_s , and D_w as follows^{20, 21}

$$\Psi = Q_1 |t|^{2-\alpha} + Q_2 |t|^{3-2\alpha-\beta}, \quad (3.1a)$$

$$C = C_1 |t|^\beta + C_2 |t|^{1-\alpha}, \quad (3.1b)$$

$$D_s = K_1 |t|^{-\gamma} + K_2 |t|^{\beta-1}, \quad (3.1c)$$

$$D_w = D_0 + D_1 |t|^{-\alpha} + D_2 |t|^{1-2\alpha-\beta}. \quad (3.1d)$$

We have replaced y_2 with $t (= T - T_c)$ for the sake of clarity since this substitution is appropriate in the three cases we are considering. The constants in Eqs. (3.1) are given in Table II. The constant D_0 is not derived from the scaling function \mathcal{S} , but comes instead from the background term \mathcal{G} of Eq. (2.1). Background terms have been dropped from the other expressions. The divergence in D_w tends to be weak ($\alpha \approx 0.1$), and hence the terms coming from the background may be important and measurable. The constant Q_2 and the final terms in C_2 , K_2 , and D_2 come from the expansion of x_2 given in (2.13) with the upper and lower signs applying to the critical isochore and coexistence surface, respectively. We note that the independent parameters in Table II are b_\pm^2 , Q_1 , C_1 , K_1 , and A_\pm .^{19(a)} The critical-point exponents are obtained in the usual way,¹⁵

$$\beta = (1 - a_1)/a_2, \quad (3.2a)$$

$$-\gamma = (1 - 2a_1)/a_2, \quad (3.2b)$$

$$-\alpha = (1 - 2a_2)/a_2. \quad (3.2c)$$

On the critical isotherm, $x_2 \propto x_1$, so that by using GHF properties we have (dropping all but the leading term)

$$C = |x_1|^{(1-a_1)/a_2} \mathcal{S}_1(\pm 1, 0). \quad (3.3)$$

Here the upper sign corresponds to x_1 positive and the lower sign to x_1 negative, and

$$\delta = a_1/(1 - a_1). \quad (3.4)$$

Combining (3.2) and (3.4) we observe that the usual exponent inequalities involving α , β , γ , and δ are satisfied as equalities; for example,

$$\alpha + 2\beta + \gamma = 2, \quad (3.5a)$$

$$\gamma = \beta(\delta - 1). \quad (3.5b)$$

TABLE II. Values of constants in Eq. (3.1).

$Q_1 = \mathcal{S}(A_\pm, \pm 1)$
$Q_2 = \pm (2-\alpha) b_\pm^2 A_\pm Q_1$
$C_1 = \mathcal{S}_1(A_\pm, \pm 1)$
$C_2 = b_\pm^2 [(2-\alpha)Q_1 + C_1 A_\pm (-\beta\delta \pm \beta)]$
$K_1 = \mathcal{S}_{11}(A_\pm, \pm 1)$
$K_2 = 2b_\pm^2 \beta C_1 - K_1 b_\pm^2 A_\pm (2\beta\delta \pm \gamma)$
$D_1 = (2-\alpha)(1-\alpha)Q_1 - \beta^2 C_1^2 / K_1 - C_1 \beta \delta A_\pm (1-\alpha-\beta)$
$D_2 = -b_\pm^2 D_1 [2\beta C_1 / K_1 + A_\pm (-2\beta\delta \pm \alpha)]$

Below the critical temperature, Eq. (2.19) provides some information which relates the amplitudes of the scaling function \mathcal{S} on the liquid and gas sides of the phase boundary. If we also require that the coexistence surface have an asymptotically symmetric top, then

$$\mathcal{S}_1^{\text{liquid}}(x_1, x_2) = -\mathcal{S}_1^{\text{gas}}(x_1, x_2), \quad (3.6)$$

at least to lowest order, on the coexistence curve. Similarly, if the strongly divergent quantities are to have the same leading-term behavior in the two phases, we must require

$$\mathcal{S}_{11}^{\text{liquid}}(x_1, x_2) = \mathcal{S}_{11}^{\text{gas}}(x_1, x_2), \quad (3.7)$$

to leading order.^{22(a)} Note that (2.15) is the only relationship between x_1 and x_2 which allows (3.6) and (3.7) to hold exactly.

Using (2.19), (3.6), and (3.7), we can evaluate the asymmetries across the phase boundary:

$$C^{\text{liquid}} + C^{\text{gas}} = 2b_1^2 Q_1 (2 - \alpha) |t|^{1-\alpha}, \quad (3.8a)$$

$$D_s^{\text{liquid}} - D_s^{\text{gas}} = 4b_1^2 \beta C_1^{\text{liquid}} |t|^{\beta-1}, \quad (3.8b)$$

$$D_w^{\text{liquid}} - D_w^{\text{gas}} = -2C_1^{\text{liquid}} (A_- \beta \delta (1 - \alpha - \beta) |t|^{-\alpha} + b_1^2 |t|^{1-2\alpha-\beta} \times \{ \beta \delta (1 - \alpha - \beta) (2\beta \delta + \alpha) A_-^2 + 2\beta [(2 - \alpha)(1 - \alpha) Q_1 - \beta^2 C_1^2 / K_1] / K_1 \}). \quad (3.8c)$$

Observe that the asymmetries in (3.8a) and (3.8b) are proportional to b_1^2 . If $b_1^2 = 0$, then the implied symmetry leads to a rectilinear diameter as is the case in the original Widom formulation. This is also true of the *weaker* asymmetry in (3.8c); however, the *leading* asymmetry depends only on A_- . If A_- is nonzero, the *amplitudes of the weak divergence differ in the liquid and gas phases*.^{22(b)} Thus, although we can maintain symmetry in the order parameter and the strong divergence, $\theta = \alpha + \beta$ breaks the symmetry of the weak divergence, typically, the specific heat.

The expressions given in Table II have one unfortunate consequence. On the critical isochore, setting $C_1 = C_2 = 0$ implies $D_1 = 0$. That is, there is no α singularity of the specific heat. The difficulty arises because we have implicitly assumed that the isochore is a natural path in the same sense that the coexistence surface is a natural path. This is not the case in an asymmetric system. The most natural order parameter ϕ is not simply the density or entropy, but some function of ρ and s given by

$$\phi = \frac{\partial \Psi}{\partial x_1}. \quad (3.9)$$

Lines of constant ϕ might be expected to be scaling invariant. If, however, we wish to describe

TABLE III. Values of constants in Eq. (3.13).

$Q'_1 = \mathcal{S}(A_+, 1)$
$Q'_2 = b_1^2 (2 - \alpha) A_+ Q'_1$
$K'_1 = \mathcal{S}_{11}(A_+, 1)$
$K'_2 = -b_1^2 [A_+ K'_1 (2\beta \delta + \gamma) + (2 - \alpha) \mathcal{S}_{111}(A_+, 1) Q'_1 / K'_1]$
$D'_1 = (2 - \alpha)(1 - \alpha) Q'_1$
$D'_2 = b_1^2 D'_1 A_+ [2\beta \delta - \alpha + \beta \delta (1 - \alpha - \beta) / (1 - \alpha)]$

the isochore, we cannot expect that path to be scaling invariant as well. We could abandon revised scaling and add correction terms to the equation of state (2.1). If, however, we retain revised scaling, we find on the isochore

$$-b_1^2 x_2^{1-\alpha-\beta} = \frac{\mathcal{S}_1(x_1/x_2^{\beta \delta}, 1)}{\mathcal{S}_2(x_1/x_2^{\beta \delta}, 1)}. \quad (3.10)$$

Inverting this equation we find that

$$x_1/x_2^{\beta \delta} = f(x_2^{1-\alpha-\beta}). \quad (3.11)$$

Since we have neglected background terms and excluded corrections to scaling, we are only justified in expanding the right-hand side of Eq. (3.11) to first order in $x_2^{1-\alpha-\beta}$. Using the explicit forms given in (3.10) we discover that on the isochore,

$$\mathcal{S}_1(A_+, 1) = 0, \quad (3.12a)$$

$$x_1 = A_+ x_2^{\beta \delta} - \frac{b_1^2 (2 - \alpha) \mathcal{S}(A_+, 1) x_2^{3-2(\alpha+\beta)}}{\mathcal{S}_{11}(A_+, 1)}. \quad (3.12b)$$

Since (3.12b) is not a scaling-invariant relationship for $b_1^2 \neq 0$, the arguments of \mathcal{S}_i and \mathcal{S}_{ij} will no longer be constant; the expansion of these amplitudes gives corrections of the same order as the corrections due to revised scaling. Employing (3.12b), we write for the critical isochore only

$$\Psi = Q'_1 |t|^{2-\alpha} + Q'_2 |t|^{3-2\alpha-\beta}, \quad (3.13a)$$

$$D_s = K'_1 |t|^{-\gamma} + K'_2 |t|^{\beta-1}, \quad (3.13b)$$

$$D_w = D_0 + D'_1 |t|^{-\alpha} + D'_2 |t|^{1-2\alpha-\beta}. \quad (3.13c)$$

The constants are given in Table III. All the formulas given in this section are special cases of the equations developed in Appendix C (cf. Tables IV–VI).

In the case of $\mu - t$ scaling of the pressure (3.12) gives the following expression for the pressure on the critical isochore ($T > T_c$):

$$\begin{aligned} p = & (\text{const})t + (\text{const}')t^2 + Q_1 t^{2-\alpha} \\ & + b_1^2 Q_1 A_+ (2 - \alpha) t^{3-2\alpha-\beta} + \rho_c A_+ t^{2-\alpha-\beta} \\ & - \rho_c b_1^2 \left(\frac{Q_1 (2 - \alpha)}{K_1} - A_+^2 (2 - \alpha - \beta) \right) t^{3-2(\alpha+\beta)}. \end{aligned} \quad (3.14)$$

An expression of this form with $A_+ = 0$ and the coefficient of the last term unrelated to δ follows from a correction to the scaling approach as well.²³

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APPENDIX A: PROPERTIES OF GENERALIZED HOMOGENEOUS FUNCTIONS

In this appendix we will develop some properties of generalized homogeneous functions (GHF's) necessary to the body of the work. We will always be discussing a GHF, $F(x_1, \dots, x_n)$,

$$\lambda^{a_f} F(x_1, \dots, x_n) = F(\lambda^{a_1} x_1, \dots, \lambda^{a_n} x_n). \quad (\text{A1})$$

Since thermodynamic functions are often evaluated along particular paths (such as the isochores and isotherms), the behavior of GHF's along different paths is crucial. The simplest path is one along a variable axis, that is, a path on which all the variables except one, x_j , are zero. On such a path, F is given by

$$F(x_1, \dots, x_n) = |x_j|^{a_f/a_j} F(0, 0, \dots, \text{sgn} x_j, 0, \dots). \quad (\text{A2})$$

This homogeneous description¹¹ gives a pure power-law behavior. However, there are many other paths that give a pure power-law dependence. If we write F as

$$F(x_1, \dots, x_n) = |x_j|^{a_f/a_j} F(x_1/|x_j|^{a_1/a_j}, \dots, \text{sgn} x_j, \dots, x_n/|x_j|^{a_n/a_j}), \quad (\text{A3})$$

we recognize a class of paths which we term *scaling-invariant paths*, which are characterized by

$$x_k = A_k |x_j|^{a_k/a_j}, \quad k \neq j. \quad (\text{A4})$$

On such a path we have the simple power-law dependence of the homogeneous paths

$$F(x_1, \dots, x_n) = |x_j|^{a_f/a_j} F(A_1, \dots, \text{sgn} x_j, \dots, A_n). \quad (\text{A5})$$

However, there is a still larger class of paths which give essentially the same behavior as (A4). If on a path we can write

$$x_k = A_k |x_j|^{a_k/a_j} + B_k |x_j|^{a_k/a_j + a_k}, \quad (\text{A6})$$

with $a_k > 0$, and if F is sufficiently nice (analytic)

near $(A_1, A_2, \dots, \text{sgn} x_j, \dots, A_n)$ we would expect (A5) to hold approximately. We would write

$$F(x_1, \dots, x_n) = |x_j|^{a_f/a_j} \times \left(F(A_1, \dots, A_n) + \sum_{k \neq j} \frac{\partial F(A_1, \dots, A_n)}{\partial x_k} B_k |x_j|^{a_k} \right). \quad (\text{A7})$$

Equation (A7) has (A5) as its leading term. We will term paths such as given in (A6) as *asymptotically tangent to the x_j axis*. Note that in the case of scaling-invariant paths (A4), the path is asymptotically tangent to all the axes with nonzero A_k .

An example of particular interest is the "straight line," for which the path is described by a linear parametrization,

$$x_k = c_k x_j. \quad (\text{A8})$$

Then if $a_j > a_k$, for all k such that $c_k \neq 0$, the path is asymptotically tangent to the x_j axis since $1 = a_k/a_j + 1 - a_k/a_j$ and, by assumption, $1 - a_k/a_j > 0$.

The variables employed in (A1) and in the body of this work may seem arbitrary and unconnected to the thermodynamic variables one is accustomed to. If we make a change of variables from (x_1, x_2, \dots, x_n) to (y, x_2, \dots, x_n) with $y = y(x_1, x_2, \dots, x_n)$ we cannot expect the GHF F to remain a GHF. Writing \bar{F} for F as a function of (y, x_2, \dots, x_n) , the statement that \bar{F} is still a GHF, i.e.,

$$\lambda^{a_f} \bar{F}(y, x_2, \dots, x_n) = \bar{F}(\lambda^{a_y} y, \lambda^{a_2} x_2, \dots, \lambda^{a_n} x_n), \quad (\text{A9})$$

is equivalent to the following differential equation for $y(x_1, x_2, \dots, x_n)$:

$$(\Delta y + \bar{\Delta} y) \Big/ \frac{\partial y}{\partial x_1} = \bar{\Delta} F \Big/ \frac{\partial F}{\partial x_1} \quad (\text{A10})$$

where the differential operators Δ and $\bar{\Delta}$ are defined by

$$\Delta = a_y - \sum_{j=1}^n a_j x_j \frac{\partial}{\partial x_j}, \quad (\text{A11})$$

$$\bar{\Delta} = \sum_{j=2}^n (a_j - \bar{a}_j) x_j \frac{\partial}{\partial x_j}. \quad (\text{A12})$$

From (A10)–(A12) we see that if the transformation leaves the basic scaling exponents unchanged along paths asymptotically tangent to the x_j axes ($j \geq 2$), that is, $a_j = \bar{a}_j$, then y satisfies the homogeneous equation¹¹

$$\Delta y = 0. \quad (\text{A13})$$

The solutions of (A13) are GHF's,

$$\lambda^{a_j} y(x_1, \dots, x_n) = y(\lambda^{a_1} x_1, \dots, \lambda^{a_n} x_n). \quad (\text{A14})$$

The converse is not true. If we rewrite (A10) as

$$\frac{\partial F}{\partial y} \Delta y = \hat{\Delta} F, \quad (\text{A15})$$

where the new differential operator, $\hat{\Delta}$, is given by

$$\hat{\Delta} = \sum_{j=2}^n (a_j - \bar{a}_j) x_j \left(\frac{\partial}{\partial x_j} \right)_y, \quad (\text{A16})$$

we see that y , a GHF, implies that $\hat{\Delta} F = 0$. This always has the trivial solution $y = F$.

In general, the right hand side of (A10) is a GHF W such that

$$\lambda^{a_1} W(x_1, \dots, x_n) = W(\lambda^{a_1} x_1, \dots, \lambda^{a_n} x_n). \quad (\text{A17})$$

Now if y is taken to be an analytic function of (x_1, \dots, x_n) , then W must also be analytic. The right-hand side of (A10) is analytic only if

$$n_j a_j = a_1, \quad (\text{A18})$$

for some integers n_j . Furthermore, if the transformation is linear, then the left hand side of (A10) is linear and we must have $n_j = 1$, or $a_j = a_1$ for all j .

If we consider a linear transformation

$$y = x_1 + \sum_{j=2}^n c_j x_j,$$

we can expand F to yield

$$F = F(y, x_2, \dots, x_n) - \sum_{j=2}^n c_j x_j \frac{\partial F}{\partial x_1}(y, x_2, \dots, x_n). \quad (\text{A19})$$

$$\begin{aligned} W_1 = & \Psi_1 \Psi_{11} (b_{11}^1 b_2^1 b_2^1 + b_{22}^1 b_1^1 b_1^1 - 2b_{12}^1 b_1^1 b_2^1) + 2\Psi_1 \Psi_{12} [b_{11}^1 b_2^1 b_2^2 + b_{22}^1 b_1^1 b_2^2 - b_{12}^1 (b_1^1 b_2^2 + b_2^1 b_2^1)] \\ & + \Psi_1 \Psi_{22} (b_{11}^1 b_2^2 b_2^2 + b_{22}^1 b_1^2 b_1^2 - 2b_{12}^1 b_1^2 b_2^2) + \Psi_1 \Psi_1 (b_{11}^1 b_{22}^1 - b_{12}^1 b_{12}^1) + \frac{1}{2} \Psi_1 \Psi_2 (b_{11}^1 b_{22}^1 + b_{11}^1 b_{22}^2 - 2b_{12}^1 b_{12}^2), \end{aligned} \quad (\text{B4a})$$

$$W_2 = W_1, \quad 1 \neq 2. \quad (\text{B4b})$$

The b_j^i and b_{jk}^i must be understood to be smooth functions of y_1 and y_2 so that the singularity structure of D_s , for example, is given by

$$\begin{aligned} D_s = & k_0 + k_1 |t|^{-\gamma} + k_2 |t|^{\beta-1} + k_3 |t|^{-\alpha} \\ & + k_4 |t|^{\beta} + k_5 |t|^{1-\alpha} + k_6 |t|^{1-\gamma}. \end{aligned} \quad (\text{B5})$$

The constant k_6 comes entirely from the t dependence of $b_1^1 b_1^1$; the constants k_4 and k_5 are a mixture of b_{11}^1 and b_{11}^2 , on the one hand, and the t dependence of $b_1^1 b_2^1$ and $b_1^2 b_2^1$, on the other. Terms like the $1-\gamma$ divergent term k_6 in (B5) could also arise by replacing the scaling function in (2.1) with

From (A19) we see that if $a_1 < a_j$ for all j such that $c_j \neq 0$, then the correction terms generated are weaker than the leading term, and that, conversely, if $a_1 > a_k$ for some k such that $c_k \neq 0$, then the correction term is stronger than the original term. Therefore, linear (and, in general, smooth transformations with a nonvanishing linear part) variable changes can only involve variables stronger than the variable undergoing transformation. The strongest variable cannot be changed at all, the second strongest can have mixtures of the strongest added to it, the third strongest, mixtures of the first and second, and so forth, down to the weakest variable, which can be considered as arbitrary.

APPENDIX B: EXACT FORMS OF C , D_w , AND D_s

From the definitions it is straightforward to obtain

$$C = b_1^1 \Psi_1 + b_1^2 \Psi_2, \quad (\text{B1})$$

$$D_s = b_1^1 b_1^1 \Psi_{11} + 2b_1^1 b_1^2 \Psi_{12} + b_1^2 b_1^2 \Psi_{22} + b_{11}^1 \Psi_1 + b_{11}^2 \Psi_2, \quad (\text{B2})$$

$$D_w = [J^2 (\Psi_{11} \Psi_{22} - \Psi_{12} \Psi_{12}) + W_1 + W_2] / D_s, \quad (\text{B3})$$

where

$$b_{jk}^i \equiv \frac{\partial^2 x_i}{\partial y_j \partial y_k}.$$

The quantities W_1 and W_2 are given by the lengthy expressions

the product of a smooth function of y_1 and y_2 and the same scaling function. This is related to the idea employed by Domb²⁴ to generate corrections to scaling for the Ising ferromagnet.

The detailed dependence of D_w as expressed in W_1 and W_2 in (B4) is very complicated and generally unenlightening. Each term is proportional to second derivatives of the transformation between (y_1, y_2) and (x_1, x_2) which, unlike the first derivatives, we have no method of estimating. A change of variables which changed the second derivatives (but left the first derivatives unchanged) leads to the generation of a series of corrections to the

scaling equation that are always weaker than the original scaling function. Therefore, if we are willing to carry correction terms of that type, we may choose the second derivatives in any way we wish.

We observe that if $\alpha + \beta < \frac{1}{2}$, the leading singular term in W_1 is in fact larger than the $|t|^{1-2\alpha+\beta}$ term discussed in Sec. III and Appendix C. We write D_w as

$$D_w = D_0 + D_1 |t|^{-\alpha} + D_2 |t|^{1-2\alpha-\beta} + D_3 |t|^{q-\alpha} + D_4 |t|^\beta. \quad (B6)$$

The new constant D_4 is given by

$$D_4 = C_1 (b_{11}^1 b_2^1 b_2^1 + b_{22}^1 - 2b_{12}^1 b_2^1). \quad (B7)$$

Since it is proportional to C_1 , the $|t|^\beta$ term vanishes on the critical isochore ($T > T_c$).

APPENDIX C: EXTENSIONS OF REVISED SCALING

The symmetry requirements on the coexistence surface [cf. Eqs. (2.19), (3.6), and (3.7)] preclude any modification of the scaling-invariant form (2.15) without a corresponding modification of the fundamental equation (2.1). That is, corrections to scaling must be added. To illustrate what can be done in a corrections-to-scaling approach, we replace (2.1) with

$$\Psi = \mathfrak{S} + \tilde{\mathfrak{S}} + \mathfrak{G}, \quad (C1)$$

where $\tilde{\mathfrak{S}}$ is a correction-to-scaling term.⁸ We restrict ourselves to a single correction term for simplicity; the further generalization is only an algebraic complication. We have no *a priori* reason to restrict $\tilde{\mathfrak{S}}$ in any way. However, for sim-

licity, we assume that $\tilde{\mathfrak{S}}$ is a GHF in the same scaling variables as \mathfrak{S} ,

$$\lambda^{1+qa_2} \tilde{\mathfrak{S}}(x_1, x_2) = \tilde{\mathfrak{S}}(\lambda^{a_1} x_1, \lambda^{a_2} x_2). \quad (C2)$$

Note that the exponent of λ on the left-hand side of (4.2) is not 1 but $1 + qa_2$ with $q > 0$. By assumption, the dominant behavior of any thermodynamic quantity is given by \mathfrak{S} . The correction-to-scaling term $\tilde{\mathfrak{S}}$ cannot affect leading-order scaling. If we assume that $\tilde{\mathfrak{S}}$ is a GHF, we know by the discussion in Sec. II B that the weaker variable can be chosen freely; there is no loss in assuming it to be simply x_2 . The stronger variable has a natural definition as the smooth part of the coexistence surface and critical isochore, and we assume that this preferred variable can be carried over to the correction term. The scaling powers a_1 and a_2 have been chosen equal to those of the scaling function \mathfrak{S} for further simplicity. One of the scaling powers can always be so chosen (cf. Ref. 15), and if the coexistence surface or critical isochore is singular with $A_\pm \neq 0$, the usefulness of the scaling-invariant path suggests that both of the scaling powers are equal to the corresponding scaling powers of the leading-term GHF.

Correction terms of the same order as those coming from \mathfrak{S} can be generated by modifying (2.15). We write for the coexistence surface

$$x_1 = A_- |x_2|^{\beta\delta} + B_- |x_2|^{\beta\delta+q}. \quad (C3)$$

Anticipating the difficulties on the critical isochore, we write for the isochore:

$$x_1 = A_+ x_2^{\beta\delta} + B_+ x_2^{\beta\delta+q} - b_1^2 (2 - \alpha) \times \frac{\mathfrak{S}(A_+, 1)}{\mathfrak{S}_{11}(A_+, 1)} x_2^{3-2(\alpha+\beta)}. \quad (C4)$$

TABLE IV. Values of constants in Eq. (C5).

$Q_1 = \mathfrak{S}(A_-, -1)$
$Q_2 = -b_1^2 A_- (2 - \alpha) Q_1$
$Q_3 = B_- C_1 + \tilde{\mathfrak{S}}(A_-, -1)$
$C_1 = \mathfrak{S}_1(A_-, -1)$
$C_2 = b_1^2 (2 - \alpha) [Q_1 - A_- C_1]$
$C_3 = B_- K_1 + \tilde{\mathfrak{S}}_1(A_-, -1)$
$K_1 = \mathfrak{S}_{11}(A_-, -1)$
$K_2 = b_1^2 [2\beta C_1 - K_1 (2\beta\delta - \gamma)]$
$K_3 = B_- \mathfrak{S}_{111}(A_-, -1) + \tilde{\mathfrak{S}}_{111}(A_-, -1)$
$D_1 = (2 - \alpha) (1 - \alpha) Q_1 - \beta^2 C_1^2 / K_1 - C_1 A_- \beta \delta (1 - \alpha - \beta)$
$D_2 = b_1^2 D_1 [A_- (2\beta\delta + \alpha) - 2\beta C_1 / K_1]$
$D_3 = B_- C_1 [\beta (3 - 2\alpha - \beta + 2q) - (1 - \alpha + q)(2 - \alpha + q)] + \beta^2 C_1^2 K_3 / K_1^2 - 2\beta$
$\times (\beta + q) C_3 C_1 / K_1 + (1 - \alpha + q)(2 - \alpha + q) Q_3 + C_3 \beta \delta A_- (\alpha + \beta - 1)$

TABLE V. Value of the constants in Eq. (C9).

$$\begin{aligned}
\bar{C}_2 &= 2b_1^2(2-\alpha)Q_1 \\
\bar{C}_3 &= 2B_-K_1 + \bar{S}_{11}^{\text{liquid}}(A_-, -1) + \bar{S}_{11}^{\text{gas}}(A_-, -1) \\
\bar{K}_2 &= 4b_1^2\beta C_1^{\text{liquid}} \\
\bar{K}_3 &= B_-[\bar{S}_{11}^{\text{liquid}}(A_-, -1) - \bar{S}_{11}^{\text{gas}}(A_-, -1)] + \bar{S}_{11}^{\text{liquid}}(A_-, -1) \\
&\quad - \bar{S}_{11}^{\text{gas}}(A_-, -1) \\
\bar{D}_1 &= 2C_1^{\text{liquid}}A_-\beta_-(1-\alpha-\beta) \\
\bar{D}_2 &= \bar{K}_2[(2-\alpha)(1-\alpha)Q_1 - \beta^2 C_1^2/K_1]/K_1 + b_1^2 A_-(2\beta\delta + \alpha)\bar{D}_1 \\
\bar{D}_3 &= 2B_-C_1^{\text{liquid}}[\beta(3-2\alpha-\beta+2q) - (1-\alpha+q)(2-\alpha+q)] \\
&\quad + \beta^2 C_1^2 \bar{K}_3/K_1^2 - 2\beta(\beta+q)C_1^{\text{liquid}}\bar{C}_3/K_1 \\
&\quad + (C_3^{\text{liquid}} - C_3^{\text{gas}})\beta\delta(\beta+\alpha-1)A_-.
\end{aligned}$$

From our discussion of changes of variable in Sec. II B, we note that if we employ a nonzero \bar{s} with $q = 1 - \alpha - \beta$, we may set $b_1^2 = 0$.

Evaluating the consequences of (4.1) and (4.3) we find on the coexistence surface:

$$\Psi = Q_1|t|^{2-\alpha} + Q_2|t|^{3-2\alpha-\beta} + Q_3|t|^{2-\alpha+q}, \quad (\text{C5a})$$

$$C = C_1|t|^\beta + C_2|t|^{1-\alpha} + C_3|t|^{\beta+q}, \quad (\text{C5b})$$

$$D_s = K_1|t|^{-\gamma} + K_2|t|^{\beta-1} + K_3|t|^{q-\gamma}, \quad (\text{C5c})$$

$$D_w = D_0 + D_1|t|^{-\alpha} + D_2|t|^{1-2\alpha-\beta} + D_3|t|^{q-\alpha}. \quad (\text{C5d})$$

The constants in (C5) are given in Table IV. The independent parameters have increased to Q_1 , C_1 , K_1 , Q_3 , C_3 , K_3 , A_+ , and B_+ .

In the simple revised-scaling scheme of Sec. III, $p-t$ and $\mu-t$ scaling, although handled in similar ways, cannot be compatible due to the intrinsic differences in symmetry. Even a pure $|t|^\beta$ dependence in $\rho(v)$ leads to a $|t|^{2\beta}$ diameter in $v(\rho)$. However, if we set $q = \beta$, we produce $|t|^{2\beta}$ terms in C (and $|t|^{\beta-\gamma}$ terms in D_s). If we assumed that $\mu-t$ scaling were valid with a $|t|^{1-\alpha}$ density diameter, then $p-t$ scaling would also be valid if in the $p-t$ scaling formalism, the following relations between the constants of (C5) held:

$$C_3 = C_1 C_1 / V_c, \quad (\text{C6a})$$

$$K_3 = 3K_1 C_1 / V_c, \quad (\text{C6b})$$

$$D_3 = D_1 C_1 / V_c. \quad (\text{C6c})$$

These relations are particularly interesting in the case $A_- = 0$ but $B_- \neq 0$, since (C3) would then imply that the divergence of the curvature of the coexistence surface, $(\partial^2 p / \partial t^2)_v$,^{19(a)} would be characterized by an exponent θ with

TABLE VI. Values of constants in Eq. (C10).

$$\begin{aligned}
Q'_1 &= \mathcal{S}(A_+, 1) \\
Q'_2 &= b_1^2(2-\alpha)A_+Q'_1 \\
Q'_3 &= \bar{\mathcal{S}}(A_+, 1) \\
K'_1 &= \mathcal{S}_{11}(A_+, 1) \\
K'_2 &= -b_1^2[A_+K'_1(2\beta\delta + \gamma) + (2-\alpha)\mathcal{S}_{111}(A_+, 1)Q'_1/K'_1] \\
K'_3 &= B_+\mathcal{S}_{111}(A_+, 1) + \bar{\mathcal{S}}_{11}(A_+, 1) \\
D'_1 &= (2-\alpha)(1-\alpha)Q'_1 \\
D'_2 &= b_1^2 D'_1 A_+[2\beta\delta - \alpha + \beta\delta(1-\alpha-\beta)/(1-\alpha)] \\
D'_3 &= (1-\alpha+q)(2-\alpha+q)Q'_3
\end{aligned}$$

$$\theta = \alpha. \quad (\text{C7})$$

Equation (C7) gives the same value of θ as that expected in the case of a smooth coexistence surface $\mu(T)$.

The generation of new singular terms in (C5) changes the asymmetries across the coexistence surface. To evaluate the asymmetries we first observe that in addition to (2.19), (3.6), and (3.7),

$$Q_3^{\text{liquid}} = Q_3^{\text{gas}}. \quad (\text{C8})$$

We find for the asymmetries

$$C^{\text{liquid}} + C^{\text{gas}} = \bar{C}_2|t|^{1-\alpha} + \bar{C}_3|t|^{\beta+q}, \quad (\text{C9a})$$

$$D_s^{\text{liquid}} - D_s^{\text{gas}} = \bar{K}_2|t|^{\beta-1} + \bar{K}_3|t|^{q-\gamma}, \quad (\text{C9b})$$

$$D_w^{\text{liquid}} - D_w^{\text{gas}} = \bar{D}_1|t|^{-\alpha} + \bar{D}_2|t|^{1-2\alpha-\beta} + \bar{D}_3|t|^{q-\alpha}. \quad (\text{C9c})$$

The constants in (C9) are given in Table V. We observe that the amplitudes of the asymmetries arising from the correction term cannot be evaluated in terms of the amplitudes of the leading-order singularities. The amplitude \bar{D}_3 can be expressed in terms of leading-term amplitudes and \bar{C}_3 and \bar{K}_3 . \bar{C}_3 and \bar{K}_3 , on the other hand, involve derivatives of \mathcal{S} and $\bar{\mathcal{S}}$ which do not play a part in any of the other amplitudes. Therefore, only the difficult measurement of C_3 , K_3 , and \bar{D}_3 can give a test of this extended revised-scaling approach.

On the critical isochore, Eqs. (C1) and (C4) combine to give

$$\Psi = Q'_1 t^{2-\alpha} + Q'_2 t^{3-2\alpha+\beta} + Q'_3 t^{2-\alpha+q}, \quad (\text{C10a})$$

$$D_s = K'_1 t^{-\gamma} + K'_2 t^{\beta-1} + K'_3 t^{2-\gamma}, \quad (\text{C10b})$$

$$D_w = D_0 + D'_1 t^{-\alpha} + D'_2 t^{1-2\alpha-\beta} + D'_3 t^{q-\alpha}. \quad (\text{C10c})$$

The constants in Eq. (C10) are given in Table VI.

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- ¹¹We use homogeneous in the sense of the vanishing of a constraint. That is, $x=0$ is a homogeneous constraint on x ; $x=F(y)$ is inhomogeneous.
- ¹²By smooth we mean having a sufficient number of continuous derivatives to avoid any difficulties.
- ¹³Near the critical point a weak singularity might not be noticeable; as we move away from the critical point the spurious ridge of singularities coming from the variable change would become relatively more important. We might accept this unphysical behavior away from the critical region in order to simply describe the critical region.
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- ¹⁶This terminology corresponds to the fact that if we take n successive derivatives of (2.2) with respect to x_1 , the exponent of λ appearing on the left-hand side of (2.2) (i.e., the scaling power of the function $\partial^n \mathcal{S} / \partial x_1^n$) changes from 1 to $1-na_1$. Then the critical-point exponent for this function is $(1-na_1)/a_1$ or $(1-na_1)/a_2$, if the path is asymptotically tangent to the x_1 or x_2 axis, respectively (see Appendix A). These exponents are algebraically smaller than the corresponding exponents obtained by differentiating \mathcal{S} with respect to x_2 , and, hence, we say that the x_1 derivatives diverge more strongly.
- ¹⁷P. Schofield, *Phys. Rev. Lett.* **22**, 608 (1969).
- ¹⁸J. F. Nicoll and H. E. Stanley (report of work prior to publication). Equation (2.7) is derived by expressing the derivative on the right-hand side by a ratio of Jacobians,
- $$\left(\frac{\partial y_1}{\partial y_2}\right)_C = \frac{\partial(y_1, C) / \partial(x_1, x_2)}{\partial(y_2, C) / \partial(x_1, x_2)}.$$
- Writing C as $b_1^2 \mathcal{S}_1 + b_2^2 \mathcal{S}_2$ and expanding the resulting Jacobians, we obtain (2.7) directly from the scaling hypothesis (since $a_1 > a_2$).
- ¹⁹(a) Experimental evidence seems to indicate that $(\partial^2 \mu / \partial T^2) \rho$ is not singular, leading to the suggestion that $\theta = \alpha$. For description of relevant experimental work, see, for example, M. Vicentini-Missoni and J. M. H. Levelt-Sengers, *J. Res. Natl. Bur. Stds. A* **73**, 563 (1969); and J. M. H. Levelt-Sengers and S. C. Greer, *Int. J. Heat Mass Transfer* **15**, 1865 (1972), J. M. H. Levelt-Sengers and W. T. Chen, *J. Chem. Phys.* **56**, 595 (1972), and references contained therein. If the possibility of $\theta = \alpha + \beta$ is excluded, then we expect that there is a hidden symmetry (similar to the $H \rightarrow -H$ symmetry in magnetic systems) in the fundamental interactions. In our formalism, this is expressed as a lowest-order symmetry by $A_+ = 0$. (b) We may write (2.19) as $\mathcal{S}_1^{\text{liquid}}(x_1/x_2^{\beta\delta}, -1) = \mathcal{S}_1^{\text{gas}}(x_1/x_2^{\beta\delta}, -1)$. If (2.15) holds, the arguments of the functions are constants; if (2.15) does not hold, then the above equation would hold for a range of values of the arguments. This is clearly impossible since, for example, we show in Sec. III that $\mathcal{S}_1^{\text{liquid}} = -\mathcal{S}_1^{\text{gas}}$ on the coexistence surface.
- ²⁰A discussion of some of the weaker singularities is given in Appendix B.
- ²¹The value for D_1 given in Ref. 9 differs from that given here because we have evaluated the weak divergence along the coexistence surface rather than on the critical isochore ($T < T_c$) as in Ref. 9. The isochore value is $D_1^{\text{iso}} = (1-\alpha)(2-\alpha)Q$, independent of A_- .
- ²²(a) In Appendix C we show that if (2.15) is not used, we can only require that the leading-order behavior correspond to the symmetries given in (3.6) and (3.7). (b) If the amplitudes of the weak divergence do not differ in the liquid and gas phases, then the implied symmetry requires $A_- = 0$, which in turn indicates $\theta < \alpha + \beta$.
- ²³See Ref. 8, Table II.
- ²⁴C. Domb, in *Critical Phenomena*, edited by M. S. Green (Academic, London, 1971).