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 ($\alpha$-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 $|T - T_c|^{1-2\alpha+\beta}$ is predicted for the isochore, which may be dominated by stronger singularities.

I. INTRODUCTION

The original scaling hypothesis was made by Widom (and, independently, by others) 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 diameter in certain models and by recent renormalization-group calculations; the singularity behaves like $|T - T_c|^{1-\alpha}$, where $\alpha (\alpha > 0)$ is the exponent characterizing the divergence of the specific heat, $C_V$. Mermin and Rehr have suggested that this $(1 - \alpha)$ singularity may be expected generally in fluids.

To incorporate the diameter singularity, Cook and Green 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 Mermin have shown that the singular diameter can be derived from a simple modification of the original scaling equation.

In 1965, Griffiths derived the rigorous inequality $\theta < \alpha + \beta$, where $\theta$ is the exponent characterizing the divergence of the curvature of the vapor pressure curve, $\Theta^2P/\Theta T^2$. 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 consequences 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 $\theta < \alpha + \beta$ 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 Widom:

(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 $\mu$ and $T$, where $\mu$ 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 $\rho$ 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 $\rho$ 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 \( T_e \), where \( \mu(T) \) describes the coexistence surface for \( T < T_e \), and the critical isochore for \( T > T_e \). The choice of \( T \) as the second variable instead of some combination of \( \mu \) and \( T_e \), coupled with Widom's use of a single scaling function, has the consequence that the density diameter is rectilinear (cf. Sec. III). The \(|T - T_e|^{-\alpha}\) dependence of the diameter can be obtained in two ways (a) by allowing the second variable to be a function of \( \mu \) and \( T_e \), and (b) by adding correction terms to the scaling equation. As we will see in Sec. III, the amplitude of the \(|T - T_e|^{-\alpha}\) 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 Merminga 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 homogeneous 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 homogeneous 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 smooth 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 \( T = T_e \) even away from the critical point. This behavior is undesirable although perhaps tolerable if the singularity were sufficiently weak. Since the singularity in the vapor pressure \( P(T) \) [and its critical isochore continuation for \( T > T_e \)] is expected to be strong, having a divergent curvature, \( (\partial^2 P/\partial T^2)_{c} \to \infty \) as \( T \to T_c \), there has been a nearly universal avoidance of \( p - t \) scaling of \( G \). (Here we utilize the reduced variables, \( p = P/P_e \) and \( t = T - T_e \).) In this work we weaken Widom's assumption to allow inhomogeneous descriptions of the critical isochore and coexistence surface in order to encompass 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 Merminga gives only the qualitative nature of the diameter, but cannot correctly predict the amplitude.

In Sec. II A we introduce a general potential \( \Psi \) 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. II B 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, 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.

In Sec. II C 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 \( x_1 = A x_2^{\delta} \) 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, \( (\partial^2 P/\partial T^2)_{c} \to \infty \), characterized by an exponent \( \delta = \alpha + \beta \), 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 symmetries, such as the diameter, utilizing the scaling-invariant parametric form \( x_1 = A x_2^{\delta} \) 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 \( \Psi \) which can be expected to scale. By keeping \( \Psi \) general, we can discuss \( p-t \) and \( \mu-t \) 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 \( \Psi \) with one scaling function and we employ initially arbitrary scaling variables. In the simple case of a single function, we write

\[
\Psi = \mathcal{S} + \mathcal{B},
\]

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

\[
\lambda \mathcal{S}(x_1, x_2) = \mathcal{S}(\lambda^a_1 x_1, \lambda^a_2 x_2),
\]

and \( \mathcal{B}(x_1, x_2) \) is a \( C^\infty \) 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 \( a > a_1 \) labels \( x_1 \) and \( x_2 \) as the strong and weak variables of Griffiths and Wheeler.\(^{14,15}\) 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 Schofield\(^{17}\) 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 \( D_{\mu} \), a typical weakly divergent quantity.\(^{14}\) In terms of the potential \( \Psi \), these are given by

\[
C = \Psi^1, \quad (2.3)
\]
\[
D_s = \Psi^{11}, \quad (2.4)
\]
\[
D_{\mu} = (\Psi^{11} \Psi^{12} - \Psi^{11} \Psi^{11})/\Psi^{11}; \quad (2.5)
\]

we introduce the notation

\[
F_i = \frac{\partial F}{\partial y_i}; \quad F = \frac{\partial F}{\partial x_i}. \quad (2.6)
\]

Table I lists the specific symbols for \( \Psi, C, D_s, y_1, y_2, \) and \( D_{\mu} \) 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 show\(^{18}\) that the scaling hypothesis (2.2) implies that near the critical point

\[
\frac{b_1}{b_2} = \frac{b_1}{b_2}, \quad (2.7)
\]

where we use the notation

\[
\frac{b_1}{b_2} \equiv \left( \frac{\partial y_1}{\partial y_2} \right)_C.
\]

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**Table I.** Symbols of values used in the text in three cases. Symbols not defined in the text are \( s = S/N \) (entropy density) and \( K_p \), the isothermal compressibility.

<table>
<thead>
<tr>
<th></th>
<th>( \mu - t ) scaling</th>
<th>( p - t ) scaling</th>
<th>Magnetic system</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Psi )</td>
<td>( P - P_c - \rho_c (\mu - \mu_c) )</td>
<td>( G - G_c + (T - T_c) S_c )</td>
<td>( G - G_c + (T - T_c) S_c )</td>
</tr>
<tr>
<td>( y_1 ) ( \mu - \mu_c )</td>
<td>( p = P - P_c )</td>
<td>( t = T - T_c )</td>
<td>( t = T - T_c )</td>
</tr>
<tr>
<td>( y_2 ) ( T = T - T_c )</td>
<td>( \rho = \rho_c )</td>
<td>( v = V - V_c )</td>
<td>( -M )</td>
</tr>
<tr>
<td>( C ) ( \rho = \rho_c )</td>
<td>( \rho )</td>
<td>( \frac{\partial \rho}{\partial P}_T )</td>
<td>( -\chi_{\rho} = -\left( \frac{\partial M}{\partial H} \right)_T )</td>
</tr>
<tr>
<td>( D_s ) ( \rho )</td>
<td>( C_V / T )</td>
<td>( -C_V / T )</td>
<td>( -C_V / T )</td>
</tr>
<tr>
<td>( \left( \frac{\partial y_1}{\partial y_2} \right)_C )</td>
<td>( \frac{\partial \mu}{\partial T}_P )</td>
<td>( \frac{\partial P}{\partial T}_V )</td>
<td>( \frac{\partial T}{\partial H} )</td>
</tr>
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</table>
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 Wheeler\(^{14}\) (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, \( \delta \); 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 \( x_2 = x_3 - (\text{const})x_1 \), our GHF, \( \delta(x_1, x_2) \), can be expanded as a sum of GHF's:

\[
\delta(x_1, x_2) = \delta(x_1, x_3) + (\text{const})x_1 \delta(x_1, x_2) + \ldots.
\]

Equation (2.9) is a series of correction terms of the form suggested\(^8\) 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

\[
|X_2|^{1-\alpha+\alpha_1}/\alpha_2 Q \left( \frac{x_1}{|X_2|^{\alpha_2}} \right) = |X_2|^{2-\alpha+\alpha_1} \delta^{\alpha-1} Q \left( \frac{x_1}{|X_2|^{\alpha_2}} \right) \tag{2.10}
\]

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, \( \delta \). 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 scaling\(^8\) 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 approach\(^8\) which leaves the weak amplitudes independent of the leading-term amplitudes. If revised scaling\(^8\) 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 \(\Gamma\),

\[
\frac{dx_2}{dy_2} \bigg|_\Gamma = \frac{J}{b_1^2 - b_1^2 d(x_1/dx_2)_{\Gamma}},
\]

(2.11)

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

\[
J = b_1^2 b_2^2 - b_1^4 b_2^4.
\]

(2.12)

We assume that \(J\) is nearly constant near the critical point; this is consistent with our assumption of a \(C^\infty\) transformation. For convenience we will normalize our variables so that at the critical point \(J = 1\) and \(b_1^2 = 1\).

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

\[
x_2 = y_2 + b_1^2 x_1(x_1).
\]

(2.13)

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

C. Forms of the coexistence surface and critical isocline

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

On all paths passing through the critical point, the singularities of \(\Psi\) in (2.1) are assumed to come from terms involving \(\delta\). We know from (2.7) that \(x_1 = 0\) on both the critical isocline and coexistence surface. Using the properties of GHP's we write for \(\delta_1\) and \(\delta_{11}\):

\[
\delta_1(x_1, x_2) = x_2^{(1-x_2)/a_2} \delta_1(x_1/x_2)^{a_1/a_2} \pm 1.
\]

(2.14a)

\[
\delta_{11}(x_1, x_2) = x_2^{(1-x_1-x_2)/a_2} \delta_{11}(x_1/x_2)^{a_1/a_2} \pm 1.
\]

(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:

\[
x_1 = A_1 \left( x_2 \right)^{a_1/a_2} = A_1 \left( x_2 \right)^{\delta_1}.
\]

(2.15)

In (2.15), \(A_1\) 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, \(A_1 = 0\), reduces to the homogeneous relation \(x_1 = 0\), corresponding to a smooth form for the phase boundary and critical isocline. The case of \(A_1 \neq 0\) gives a power-law singularity. We observe that on any path \(\Gamma\),

\[
\frac{dy_1}{dy_2} \bigg|_\Gamma = -b_1^2 \pm \frac{b_1^2}{\left( \frac{dx_1}{dx_2} \right)_{\Gamma}^{\frac{\alpha}{a_2}} \left( \frac{dx_2}{dy_2} \right)_{\Gamma}^{-\frac{\delta_1}{a_2}}},
\]

(2.16)

The \(b_1^2\) are smooth by assumption and by (2.13), \((dx_1/dy_2)_{\Gamma}\) is nearly constant. We therefore expect that the curvature of the path \(dx_1/dy_2\) in a scaling-invariant path (2.15) will be given approximately by

\[
\left( \frac{dy_1}{dy_2} \right)_{\Gamma} - \left( \frac{dx_1}{dx_2} \right)_{\Gamma}^{\alpha/\gamma} |y_2|^{(1-\alpha)/a_2} - |y_2|^{\delta_1},
\]

(2.17)

where the exponent is given by

\[
\beta = \alpha + \beta.
\]

(2.18)

In both \(p-T\) and \(\mu-T\) scaling, (2.18) satisfies the inequality\(^{15}\) \(\beta < \alpha + \beta\) as an equality.\(^{16}\) 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 \(\delta\) corresponding to the liquid and gas phases. The coexistence surface is defined by the equality of \(\delta\) on these two branches; that is, on the coexistence surface,

\[
\delta_{\text{liquid}}(x_1, x_2) = \delta_{\text{gas}}(x_1, x_2).
\]

(2.19)

Only the form given in (2.15) allows (2.19) to be satisfied exactly,\(^{16}\) 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 isocline 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.\textsuperscript{13} In the $p-t$ scaling case, for example, we can write the form of the coexistence surface as

$$p - (\text{const})t - (\text{const})t^2 + \cdots = A_\infty |t|^{1-\alpha} + \cdots$$  \hspace{1cm} (2.20)

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

$$x_i = A_\infty |x_i|^{1-\alpha}.$$  \hspace{1cm} (2.21)

(4) A similar situation might exist in $\mu-t$ scaling with the possibility that $\beta < 0$.) 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 $x_i$ 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, $x_i$ 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 $C$, $D_\infty$, and $D_\omega$. We show that the use of (2.15) with $A_\infty$ nonzero changes both the leading and nonleading amplitudes and gives a leading-term ($\alpha$-divergent) liquid-gas asymmetry in $D_\omega$ 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.\textsuperscript{6}

Employing Eq. (2.15), and utilizing the properties of GFF's, we can express the quantities $\Psi$, $C$, $D_\infty$, and $D_\omega$ as follows\textsuperscript{16,21}

$$\Psi = Q_1 |t|^{1-\alpha} + Q_2 |t|^{1-2\alpha - \delta},$$  \hspace{1cm} (3.1a)

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

$$D_\infty = K_1 |t|^{-\gamma} + K_2 |t|^{\delta - 1},$$  \hspace{1cm} (3.1c)

$$D_\omega = D_\omega + D_1 |t|^{-\alpha} + D_2 |t|^{1-2\alpha - \delta}.$$  \hspace{1cm} (3.1d)

We have replaced $\gamma_0$ 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 $D_\omega$ is not derived from the scaling function $\Psi$, but comes instead from the background term $\alpha$ of Eq. (2.1). Background terms have been dropped from the other expressions. The divergence in $D_\omega$ 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 $C$, $K_2$, and $D_2$ come from the expansion of $x_i$ given in (2.15) 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 $b_0$, $Q_1$, $C_1$, $K_1$, and $A_\infty$.\textsuperscript{19,21} The critical-point exponents are obtained in the usual way,\textsuperscript{16}

$$\beta = (1 - a_1)/a_2,$$  \hspace{1cm} (3.2a)

$$\gamma = (1 - 2a_1)/a_2,$$  \hspace{1cm} (3.2b)

$$\alpha = (1 - 2a_2)/a_2.$$  \hspace{1cm} (3.2c)

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

$$C = |x_i|^{1-\alpha}/\delta A_\infty (1, 0).$$  \hspace{1cm} (3.3)

Here the upper sign corresponds to $x_i$ positive and the lower sign to $x_i$ negative, and

$$\delta = a_2/(1 - a_1).$$  \hspace{1cm} (3.4)

Combining (3.2) and (3.4) we observe that the usual exponent inequalities involving $\alpha$, $\beta$, $\gamma$, and $\delta$ are satisfied as equalities; for example,

$$\alpha + 2\beta + \gamma = 2,$$  \hspace{1cm} (3.5a)

$$\gamma = \beta(\delta - 1).$$  \hspace{1cm} (3.5b)

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

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_1$</td>
<td>$\delta (A_\infty, \pm 1)$</td>
</tr>
<tr>
<td>$Q_2$</td>
<td>$\pm (2-\alpha)K_1 A_\infty Q_1$</td>
</tr>
<tr>
<td>$C_1$</td>
<td>$\delta (A_\infty, \pm 1)$</td>
</tr>
<tr>
<td>$C_2$</td>
<td>$2b [2 \delta C_1 - K_1 b A_\infty (2\beta \delta + \gamma)]$</td>
</tr>
<tr>
<td>$K_1$</td>
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</tr>
<tr>
<td>$D_1$</td>
<td>$(2-\alpha)(1-\alpha)Q_1 b^{-\beta} C_2 K_1 C^{-1} A_\infty (1 - \beta - \alpha)$</td>
</tr>
<tr>
<td>$D_2$</td>
<td>$-b [2 \delta D_1 (2\beta C_2 K_1 A_\infty (2\beta \delta + \alpha))]$</td>
</tr>
</tbody>
</table>
Below the critical temperature, Eq. (2.19) provides some information which relates the amplitudes of the scaling function $g$ on the liquid and gas sides of the phase boundary. If we also require that the coexistence surface have an asymptotically symmetric top, then

$$ s_{1}^{\text{liquid}}(x_1, x_2) = -s_{1}^{\text{gas}}(x_1, x_2), \quad (3.6) $$

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

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

to leading order. 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:

$$ C_{s}^{\text{liquid}} + C_{s}^{\text{gas}} = 2b\left(Q_i(2 - \alpha)\right)t_1^{-1 - \alpha}, \quad (3.8a) $$

$$ D_{s}^{\text{liquid}} - D_{s}^{\text{gas}} = 4b\beta C_{1}^{\text{liquid}} t_1^{-\alpha - 1}, \quad (3.8b) $$

$$ D_{e}^{\text{liquid}} - D_{e}^{\text{gas}} = -2b\beta C_{1}^{\text{liquid}} \left(A_{1} \beta(1 - \alpha - \beta) t_1^{-\alpha - b} + b\beta(1 - 2\alpha - \beta) t_1^{-1 - 2\alpha - \beta}\right) $$

$$ \times \left(\beta(1 - \alpha - \beta)(2\beta + \alpha)A_{1}^2 + 2\beta(1 - 2\alpha - \beta)Q_i^2 - \beta^2 C_{1}^2 / K_1 / K_{1i}\right), \quad (3.8c) $$

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 rectangular diameter as is the case in the original Widom formulation. This is also the case of the weaker asymmetry in (3.8c); however, the leading asymmetry depends only on $A_{1}$. If $A_{1}$ is nonzero, the amplitudes of the weak divergence differ in the liquid and gas phases. 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 $\alpha$ 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 $\phi$ is not simply the density or entropy, but some function of $\rho$ and $s$ given by

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

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

<table>
<thead>
<tr>
<th>Table III. Values of constants in Eq. (3.13).</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{1} = b\left[Q_i(2 - \alpha)A_{1}Q_{i}^{1}\right]$</td>
</tr>
<tr>
<td>$K_{1} = \frac{b}{s_{11}(A_{1}, 1)}$</td>
</tr>
<tr>
<td>$K_{1} = -b\left[A_{1} K_{1}(2\beta + \gamma) + 2\alpha A_1 s_{11}(A_{1}, 1) Q_{1}^{1} / K_{1}\right]$</td>
</tr>
<tr>
<td>$D_{s} = (2\alpha + 1 - \alpha)Q_{i}^{1}$</td>
</tr>
<tr>
<td>$D_{e} = b\left[D_{1}(2\beta - \alpha) + \beta(1 - \alpha - \beta)/(1 - \alpha)\right]$</td>
</tr>
</tbody>
</table>

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

$$ \frac{b_{1}^{2} x_1^{1 - 1 - \alpha} - s_{1}(x_1 / x_2)^{1 - 1 - \alpha}}{s_{1}(x_1 / x_2)^{1 - 1 - \alpha}}. \quad (3.10) $$

Inverting this equation we find that

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

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 $x_2^{1 - 1 - \alpha}$. Using the explicit forms given in (3.10) we discover that on the isochore,

$$ s_{1}(A_{1}, 1) = 0, \quad (3.12a) $$

$$ x_1 = A_{1} x_2^{1 - 1 - \alpha} - \frac{b_{1}^{2}(2 - \alpha) s_{1}(A_{1}, 1) x_2^{1 - 1 - \alpha}}{s_{1}(A_{1}, 1)}. \quad (3.12b) $$

Since (3.12b) is not a scaling-invariant relationship for $b_{1} \neq 0$, the arguments of $s_{1}$ and $s_{1}$ 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

$$ \psi = Q_{1}^{1} t_1^{2 - \alpha} + Q_{1}^{1} t_1^{3 - 2\alpha - \delta}, \quad (3.13a) $$

$$ D_{s} = K_{1} t_1^{-\gamma} + K_{1} t_1^{1 - \alpha - \delta}, \quad (3.13b) $$

$$ D_{e} = D_{0} + D_{1} t_1^{2 - \alpha} + D_{2} t_1^{1 - 2\alpha - \delta}. \quad (3.13c) $$

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 ($T > T_{c}$):

$$ p = (const) t_1 + (const) t_1^2 + Q_{1} t_1^{2 - \alpha} $$

$$ + b_{1}^{2} Q_{1} A_{1} (2 - \alpha) t_1^{2 - 2\alpha - \delta} + \rho A_{1} t_1^{2 - \alpha - \delta} $$

$$ - \rho b_{1}^{1} \left(\frac{Q_{1} (2 - \alpha)}{K_{1}} - A_{1}^{1} (2 - \alpha - \beta)\right) t_1^{2(\alpha + \beta)}. \quad (3.14) $$
An expression of this form with $A_k = 0$ and the coefficient of the last term unrelated to $s$ follows from a correction to the scaling approach as well.$^{23}$

**ACKNOWLEDGMENTS**

The authors are grateful to R. V. Ditzian, F. Harbus, L. L. Liu, and G. F. Tuthill for helpful discussions in connection with this work. They also wish to thank Professor R. B. Griffiths and Professor J. C. Wheeler for useful comments at the 1972 MIT Summer School on Critical Phenomena, and Professor N. D. Mermin, Professor J. J. Rehr, Professor M. S. Green, and Professor J. M. H. Leveille-Sengers for comments on a draft of the manuscript.

**APPENDIX A: PROPERTIES OF GENERALIZED HOMOGENEOUS FUNCTIONS**

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

$$
\lambda^s F(x_1, \ldots, x_n) = \lambda^{s_1} x_1 \lambda^{s_2} x_2 \cdots \lambda^{s_n} x_n.
$$

(A1)

Since thermodynamic functions are often evaluated along particular paths (such as the isochore and isotherms), the behavior of GHFs' 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

$$
F(x_1, \ldots, x_n) = |x_j|^{s_j} F(0, 0, \ldots, s_{\text{sgn} x_j}, 0, \ldots).
$$

(A2)

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

$$
F(x_1, \ldots, x_n) = |x_j|^{s_j} F(x_1, \ldots, x_n) / |x_j|^{s_j} F(x_1, \ldots, x_n)
$$

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

$$
x_k = A_k |x_j|^{q_k / s_j}, \quad k \neq j.
$$

(A4)

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

$$
F(x_1, \ldots, x_n) = |x_j|^{s_j} F(A_1, \ldots, s_{\text{sgn} x_j}, \ldots, A_n).
$$

(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

$$
x_k = A_k |x_j|^{q_k / s_j} + B_k |x_j|^{q_k / s_j + s_k},
$$

(A6)

with $q_k > 0$, and if $F$ is sufficiently nice (analytic) near $(A_1, A_2, \ldots, s_{\text{sgn} x_j}, \ldots, A_n)$ we would expect (A5) to hold approximately. We would write

$$
F(x_1, \ldots, x_n) = |x_j|^{s_j} F(A_1, \ldots, A_n)
$$

$$
\times \left( \frac{\delta F(A_1, \ldots, A_n)}{\delta x_k} B_k |x_j|^{s_k} \right).
$$

(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,

$$
x_k = c_k x_j.
$$

(A8)

Then if $a_j = c_k$, for all $k$ such that $c_k 
eq 0$, 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 $(x_1, x_2, \ldots, x_n)$ to $(y_1, y_2, \ldots, y_n)$ with $y = y(x_1, x_2, \ldots, x_n)$ we cannot expect the GHF $F$ to remain a GHF.

Writing $\bar{F}$ for $F$ as a function of $(y_1, y_2, \ldots, y_n)$, the statement that $\bar{F}$ is still a GHF, i.e.,

$$
\lambda^s \bar{F}(y_1, y_2, \ldots, y_n) = \bar{F}(\lambda^s y_1, \lambda^s y_2, \ldots, \lambda^s y_n),
$$

(A9)

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

$$
(\Delta y + \Delta y) / \partial x_j = \Delta F / \partial x_j
$$

(A10)

where the differential operators $\Delta$ and $\Delta$ are defined by

$$
\Delta = a_j - \sum_{j=1}^{n} a_j x_j / \partial x_j,
$$

(A11)

$$
\Delta = \sum_{j=1}^{n} (a_j - \overline{a_j}) x_j / \partial x_j.
$$

(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, $a_j = \overline{a_j}$, then $y$ satisfies the homogeneous equation

$$
\Delta y = 0.
$$

(A13)

The solutions of (A13) are GHF's,
\[ \lambda^n y(x_1, \ldots, x_n) = y(\lambda^nx_1, \ldots, \lambda^nx_n). \] 
\[ \text{(A14)} \]

The converse is not true. If we rewrite (A10) as
\[ \frac{\partial F}{\partial y} \Delta y = \hat{\Delta} F, \]
\[ \text{(A15)} \]
where the new differential operator, \( \hat{\Delta} \), is given by
\[ \hat{\Delta} = \sum_{j=2}^{n} (a_j - \bar{a}_j) x_j \left( \frac{\partial}{\partial x_j} \right), \]
\[ \text{(A16)} \]
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
\[ \lambda^n W(x_1, \ldots, x_n) = W(\lambda^nx_1, \ldots, \lambda^nx_n). \]
\[ \text{(A17)} \]
Now if \( y \) is taken to be an analytic function of \( (x_1, \ldots, x_n) \), then \( W \) must also be analytic. The right-hand side of (A10) is analytic only if
\[ n_j a_j = a_1, \]
\[ \text{(A18)} \]
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
\[ F = F(y, x_2, \ldots, x_n) + \sum_{j=2}^{n} c_j x_j \frac{\partial F}{\partial x_j} (y, x_2, \ldots, x_n). \]
\[ \text{(A19)} \]

\[ W_1 = \psi_1 \psi_2 \left( b_1 b_2^3 + b_2 b_3^3 - 2 b_1 b_2 b_3^3 \right) + 2 \psi_1 \psi_2 \left( b_1 b_2^3 + b_2 b_3^3 - b_1 b_2 b_3^3 \right), \]
\[ W_2 = W_1, \text{ for all } j. \]
\[ \text{(B4a)} \]

The \( b_j^i \) and \( b_j \) must be understood to be smooth functions of \( y_1 \) and \( y_2 \) so that the singularity structure of \( D_n \), for example, is given by:
\[ D_n = k_0 + k_1 |t|^{-\gamma} + k_2 |t|^{\beta_1} + k_3 |t|^{-\alpha} \]
\[ + k_4 |t|^{\beta_2} + k_5 |t|^{1 - \alpha} + k_6 |t|^{-\gamma}. \]
\[ \text{(B5)} \]

The constant \( k_0 \) comes entirely from the \( t \) dependence of \( b_j^i b_j^i \); the constants \( k_1 \) and \( k_2 \) are a mixture of \( b_1^i b_j^i \) and \( b_2^j b_1^j \), on the one hand, and the \( t \) dependence of \( b_1^i b_2^i \) and \( b_2^j b_1^j \), 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 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 Domb\( b^{*} \) to generate corrections to scaling for the Ising ferromagnet.

The detailed dependence of \( D_n \) 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
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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 $W$, is in fact larger than the $t^{1-2 \alpha - \beta}$ discussed in Sec. III and Appendix C. We write $D_w$ as

$$D_w = D_0 + D_1 |t|^{-\alpha} + D_2 |t|^{1-2 \alpha - \beta} + D_3 |t|^{-\gamma} + D_4 |t|^{\gamma}.$$  

(B6)

The new constant $D_4$ is given by

$$D_4 = C_1 b_1 b_2 + b_1 + b_2.$$  

(B7)

Since it is proportional to $C_1$, the $|t|^\gamma$ 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

$$\psi = \bar{\psi} + \delta + \sigma,$$

(C1)

where $\bar{\psi}$ is a correction-to-scaling term. 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 $\bar{\psi}$ in any way. However, for simplicity, we assume that $\bar{\psi}$ is a GHF in the same scaling variables as $\bar{\psi}$,

$$\lambda^{1+2 \alpha} \bar{\psi}(x_1, x_2) = \bar{\psi}(\lambda x_1, \lambda x_2).$$  

(C2)

Note that the exponent of $\lambda$ on the left-hand side of (4.2) is not 1 but $1 + \alpha x_2$ with $\alpha > 0$. By assumption, the dominant behavior of any thermodynamic quantity is given by $\bar{\psi}$. The correction-to-scaling term $\delta$ cannot affect leading-order scaling. If we assume that $\bar{\psi}$ 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 $\alpha_1$ and $\alpha_2$ have been chosen equal to those of the scaling function $\bar{\psi}$ 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 $\alpha = 0$, 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 $\bar{\psi}$ can be generated by modifying (2.15). We write for the coexistence surface

$$x_1 = A_+ |x_1|^{\alpha_1} + B_- |x_2|^{\alpha_2},$$  

(C3)

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

$$x_1 = A_+ x_2^{\alpha_2} + B_+ x_2^{\alpha_2+2\alpha} - b_2 |2 - \alpha|$$

$$\times \frac{\bar{\psi}(A_+, 1)}{\bar{\psi}_1(A_+, 1)} x_2^{3-(\alpha+\beta)},$$  

(C4)

<table>
<thead>
<tr>
<th>TABLE IV. VALUES OF CONSTANTS IN EQUATION (C5).</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_1 = \bar{\psi}(A_+, 1)$</td>
</tr>
<tr>
<td>$Q_2 = -b_1 A_+ (2 - \alpha) Q_1$</td>
</tr>
<tr>
<td>$Q_3 = b_2 A_+ C_1 + \bar{\psi}(A_+, 1)$</td>
</tr>
<tr>
<td>$C_1 = \bar{\psi}<em>1(A</em>+, 1)$</td>
</tr>
<tr>
<td>$C_2 = b_1</td>
</tr>
<tr>
<td>$C_3 = b_2 A_+ K_1 + \bar{\psi}(A_+, 1)$</td>
</tr>
<tr>
<td>$K_1 = \bar{\psi}<em>1(A</em>+, 1)$</td>
</tr>
<tr>
<td>$K_2 = b_1</td>
</tr>
<tr>
<td>$K_3 = b_2 A_+ C_1 + \bar{\psi}<em>1(A</em>+, 1)$</td>
</tr>
<tr>
<td>$D_1 = (2 - \alpha) (1 - \alpha) Q_1 - \beta C_1 K_1 + C_3 A_+ \beta \delta (1 - \alpha - \beta)$</td>
</tr>
<tr>
<td>$D_2 = (b_1 d_1 + b_2 A_+ (2 \beta \delta + \alpha) - 2 \delta C_1 K_1)$</td>
</tr>
<tr>
<td>$D_3 = b_2 C_1 \beta (3 - 2 \alpha - \beta + 2 \gamma) = (1 - \alpha + q)(2 - \alpha + q)$</td>
</tr>
<tr>
<td>$\times b_2 C_1 \delta A_+ \omega + \beta - 1$</td>
</tr>
</tbody>
</table>

(continued on next page)
From our discussion of changes of variable in Sec. II B, we note that if we employ a nonzero $\bar{S}$ with $q = 1 - a - b$, we may set $b^2 = 0$. Evaluating the consequences of (4.1) and (4.3) we find on the coexistence surface:

$$\psi = Q_1 t|t|^{2-\alpha} + Q_2 t|t|^{3-2\alpha-\beta} + Q_3 t|t|^{2-\alpha+\beta}$$  \hspace{1cm} (C5a)

$$C = C_1 \frac{t}{t^{\delta-\gamma}} + C_2 \frac{t}{t^{1-\alpha+\gamma}} + C_3 \frac{t}{t^{\delta+\gamma}}$$  \hspace{1cm} (C5b)

$$D_0 = K_2 t^{\delta+\gamma} + K_3 t^{\delta-\gamma} + K_4 t^{\delta+\gamma}$$  \hspace{1cm} (C5c)

$$D_0 = D_0 + D_1 t^{1-\alpha} + D_2 t^{1-2\alpha-\delta} + D_3 t^{\delta-\alpha}$$  \hspace{1cm} (C5d)

The constants in (C5) are given in Table IV. The independent parameters have increased to $Q_1$, $C_1$, $K_1$, $Q_2$, $C_2$, $K_2$, $A_c$, and $B_0$. 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 $|t|^\delta$ dependence in $p(\rho)$ leads to a $|t|^\delta$ diameter in $\rho(p)$. However, if we set $\frac{q}{b} = \beta$, we produce $|t|^{2\delta}$ terms in $C$ and $|t|^{\delta+\gamma}$ terms in $D_0$. If we assumed that $\mu - t$ scaling were valid with a $|t|^{1-\alpha}$ density diameter, then $p - t$ scaling would also be valid in the $p - t$ scaling formalism, the following relations between the constants of (C5) held:

$$C_3 = C_4 C_5 / V_e^2$$  \hspace{1cm} (C6a)

$$K_5 = 3 K_2 C_4 / V_e^2$$  \hspace{1cm} (C6b)

$$D_3 = D_5 C_4 / V_e^2$$  \hspace{1cm} (C6c)

These relations are particularly interesting in the case $A_c = 0$ but $B_0 \neq 0$, since (C3) would then imply that the divergence of the curvature of the coexistence surface, $(\partial^2 \rho / \partial t^2)^{1003}$ would be characterized by an exponent $\delta$ with

$$\theta = \alpha.$$  \hspace{1cm} (C7)

Equation (C7) gives the same value of $\delta$ 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), (3.5), and (3.7), $Q_1^{\text{liquid}} = Q_3^{\text{gas}}$.

We find for the asymmetries

$$C_1^{\text{liquid}} + C_1^{\text{gas}} = C_2^2 t|t|^{1-\delta} + C_3^2 t|t|^{\delta+\gamma},$$  \hspace{1cm} (C9a)

$$D_0^{\text{liquid}} - D_0^{\text{gas}} = K_2 t^{\delta+\gamma} + K_3 t^{\delta-\gamma} + K_4 t^{\delta+\gamma},$$  \hspace{1cm} (C9b)

$$D_0^{\text{liquid}} - D_0^{\text{gas}} = D_1 t^{1-\alpha} + D_2 t^{1-2\alpha-\delta} + D_3 t^{\delta-\alpha}. $$  \hspace{1cm} (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 $D_0$ can be expressed in terms of leading-term amplitudes and $C_3$, $K_2$, $C_2$, and $K_3$, on the other hand, involve derivatives of $\delta$ and $\bar{S}$ which do not play a part in any of the other amplitudes. Therefore, only the difficult measurement of $C_3$, $K_3$, and $D_1$ can give a test of this extended revised-scaling approach.

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

$$\psi = Q_1 t^{2-\alpha} + Q_2 t^{3-2\alpha-\beta} + Q_3 t^{2-\alpha+\beta},$$  \hspace{1cm} (C10a)

$$D_0 = K_1 t^{\delta+\gamma} + K_2 t^{\delta-\gamma} + K_3 t^{\delta+\gamma},$$  \hspace{1cm} (C10b)

$$D_0 = D_0 t^{1-\alpha} + D_2 t^{1-2\alpha-\delta} + D_3 t^{\delta-\alpha}. $$  \hspace{1cm} (C10c)

The constants in Eq. (C10) are given in Table VI.
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5The diameter is defined as the sum of the values of the order parameter on opposite sides of the coexistence surface, that is, at the same chemical potential or pressure (for μ-T and P-T representations, respectively). For a symmetric system this sum would be a constant. In a real system we would expect to have analytic background terms. In particular, we would expect it to depend linearly on temperature, a so-called "rectilinear diameter." For fluid systems, the experimental evidence indicates that the coexistence surface is roughly symmetric in the μ-T plane; thus μ-T scaling is to be preferred over P-T scaling. See, e.g., J. M. H. Levelt-Sengers, J. Struik, and M. Vicentini-Missoni, J. Chem. Phys. 54, 5094 (1971); J. M. H. Levelt-Sengers, Physica 73, 73 (1974), and references therein.


10F. J. Cook and M. S. Green (report of work prior to publication). Many of the Cook-Green ideas were reported in M. S. Green, M. J. Cooper, and J. M. H. Levelt-Sengers, Phys. Rev. Lett. 26, 492 (1971).


13We use homogeneous in the sense of the vanishing of a constraint. That is, x = 0 is a homogeneous constraint on x; F(x) is inhomogeneous.

14By smooth we mean having a sufficient number of continuous derivatives to avoid any difficulties.

15Near 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.


18This terminology corresponds to the fact that if we take π successive derivatives of (2.2) with respect to x, the exponent of λ appearing on the left-hand side of (2.3) (i.e., the scaling power of the function d^nS/dx^n) changes from 1 to 1 - 2nπ. Then the critical-point exponent for this function is (1 - nπ), B^n, or (1 - nπ), δ^n, if the path is asymptotically tangent to the x₁ or x₂ axis, respectively (see Appendix A). These exponents are algebraically smaller than the corresponding exponents obtained by differentiating $ with respect to x, and, hence, we say that the xᵢ derivatives diverge more strongly.


20J. 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,

$$
\left( \frac{d\nu}{d\nu_1} \right) = \frac{\frac{\partial (\nu_1 \nu_2 \nu_3)}{\partial (\nu_1 \nu_2 \nu_3)}}{\frac{\partial (\nu_1 \nu_2 \nu_3)}{\partial (\nu_1 \nu_2 \nu_3)}}
$$

Writing C as $b_1S_1 + b_2S_2$ and expanding the resulting Jacobians, we obtain (2.7) directly from the scaling hypothesis (since $a_1 > a_2$).

21(a) Experimental evidence seems to indicate that $\delta\nu/\delta^{2n}\phi$ is not singular, leading to the suggestion that $\delta = \alpha$. For description of relevant experimental work, see, for example, M. Vicentini-Missoni and J. M. H. Levelt-Sengers, J. Res. Natl. Bur. Std. A 76, 565 (1969); and J. M. H. Levelt-Sengers and S. C. Greer, Int. J. Heat Mass Transfer 15, 1855 (1972), J. M. H. Levelt-Sengers and W. T. Chen, J. Chem. Phys. 56, 595 (1972), and references contained therein. If the possibility of $\delta = \alpha + \beta$ or $\delta = \alpha$ is excluded, we can 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 $A_\perp$ = 0, (b) We may write (2.19) as $\delta^{\text{bulk}} (\xi_1^x / \xi_2^y, -1) = \delta^{\text{bulk}} (\xi_1^x / \xi_2^y, -1)$. If (2.19) 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 $\delta^{\text{bulk}} = \delta^{\text{bulk}}$ on the coexistence surface.

22A discussion of some of the weaker singularities is given in Appendix B.

23The 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 $D_1 = 2(1-c)(2-c)Q$, independent of $A_\perp$.

24(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 $A_\perp$ = 0, which in turn indicates $\theta < \alpha + \beta$.

25See Ref. 8, Table II.