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Comparison of complete scaling and a field-theoretic treatment of asymmetric fluid criticality

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We investigate the connection between the theory of complete scaling and a field-theoretic (FT) treatment of asymmetric fluid criticality. To facilitate the comparison, we develop an equation of state from a simplified form of the complete scaling transformations and systematically compare this equation of state with the equation of state generated by a FT treatment of an asymmetric Landau-Ginzburg-Wilson Hamiltonian. We find, with care in interpretation, that these two approaches may be read as equivalent up to terms involving an independent higher-order asymmetric correction-to-scaling exponent.

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I. INTRODUCTION

Universality is a central feature of critical phenomena [1,2]. It is well established, primarily through experiment [3], that the liquid-vapor critical point in one-component fluids and the liquid-liquid consolute point in binary mixtures belong to the universality class of the three-dimensional (3D) Ising model. The isomorphism between members of a universality class can be established by mapping the thermodynamic variables of one system onto another. However, the choice of mapping between fluids and the Ising system is not obviously determined by thermodynamics.

The canonical mapping of the liquid-vapor critical point onto Ising criticality is given by the lattice-gas model [4]. This model can easily be extended to binary fluids and fluid mixtures through a reassignment of variables and the principle of isomorphism [5]. For the remainder of the text, we will focus on the liquid-vapor system for concreteness. The lattice-gas model preserves the exact symmetry of uniaxial Ising-type ferromagnets and, consequently, the liquid-vapor coexistence curve of the lattice gas is symmetric with respect to the density ρ. The order parameter of the lattice gas is the reduced density

\[ \rho_d = \frac{\langle n \rangle}{\rho_c}, \]

where \( \rho_c \) is the value of the number density at the critical density. If the liquid and vapor branches of the coexistence curve are denoted by “+” and “−”, respectively, the asymmetric portion of the density is given by the excess density

\[ \Delta \rho_d = \frac{\Delta \rho^+ + \Delta \rho^-}{2}. \]

For the lattice gas, \( \Delta \rho_d = 0 \). However, real fluids do not possess the symmetry of the Ising model, and in general \( \Delta \rho_d \neq 0 \). Even the coexistence curve of \(^3\)He, the most symmetric fluid known, exhibits some small asymmetry [6]. In asymmetric systems, the leading behavior is still determined by the Ising-type behavior and asymmetric corrections appear as subleading terms in quantities like the density. In mean-field models of the liquid-vapor critical point, such as the van der Waals model, the asymmetry of the coexistence curve is described by the “law” of rectilinear diameter [7]

\[ \Delta \rho_d = D_1 |\Delta \hat{T}|, \]

where the reduced temperature is defined by \( \Delta \hat{T} = (T - T_c) / T_c \), with \( T_c \) being the critical temperature. While some one-component fluids such as xenon [8] seem to asymptotically follow this “law,” others, such as SF\(_6\) [9], show strong deviations from rectilinearity in the critical region.

Models such as the Widom-Rowlinson penetrable-sphere model [10] and Mermin’s decorated-lattice models [11,12] predict nonclassical, i.e., non-mean-field, behavior of the excess density. On the basis of these models, a nonclassical theory of fluid criticality, known as “revised scaling,” [13] was proposed. The formulation of revised scaling postulates that the Ising scaling fields are analytic functions of the chemical potential \( \mu \) and temperature \( T \), whereas the lattice-gas model assumes that \( \mu \) and \( T \) are the correct scaling fields. This field mixing produces the following asymptotic behavior:

\[ \Delta \rho_d \approx D_1 |\Delta \hat{T}|^{-\alpha} + D_1 |\Delta \hat{T}|, \]

where \( \alpha \approx 0.11 \) [14] (1 – \( \alpha \approx 0.89 \)) is a universal critical exponent, which characterizes the divergence of the heat capacity.

Additional theoretical support for revised scaling came from Nicoll and Zia [15], and Nicoll [16], who performed a field-theoretic (FT) analysis of an asymmetric Landau-Ginzburg-Wilson (LGW) Hamiltonian and found that revised scaling arises naturally from the inclusion of asymmetric operators in the Hamiltonian. In addition, they found that these asymmetric operators also lead to a nonanalytic correction to the excess density characterized by a new asymmetric correction-to-scaling exponent \( \theta_5 \). The excess density predicted by their analysis goes as

\[ \Delta \rho_d \approx D_1 |\Delta \hat{T}|^{-\alpha} + D_1 |\Delta \hat{T}| + D_1 \epsilon |\Delta \hat{T}|^{\beta + \theta_5}, \]

where \( \beta \approx 0.326 \) [14]. The universal exponent \( \theta_5 \) was found to be \( \theta_5 = 1 / (1 + 0.326) = 3/2 \) in the first-order \( \epsilon \) expansion, where \( \epsilon = 4 - d \) and \( d \) is the spatial dimensionality [17,18]. Working to order \( \epsilon^3 \), Zhang and Zia [19] found their results to be consistent with the bound \( \theta_5 \geq 1.0 \).
More recently, Fisher and co-workers [20,21] have argued for an extended formulation of scaling, originally discussed by Rehr and Mermin [13], which is now known as “complete scaling.” This theory of asymmetric fluid criticality is an extension of the field mixing in revised scaling and incorporates the hypothesis of Griffiths and Wheeler [22] that preferred thermodynamic variables do not exist. This concept implies that pressure $P$, chemical potential $\mu$, and temperature $T$ should all be treated on equal footing in any formulation of scaling for the liquid-vapor critical point. The Ising scaling fields should therefore be treated as analytic functions of all three. In contrast, revised scaling assigns a special role to the pressure $P(\mu,T)$ as the field-dependent thermodynamic potential. Complete scaling predicts that the excess density is asymptotically given by

$$\Delta \rho_d \approx D \beta |\Delta T|^{2\beta} + D_{1-\alpha} |\Delta T|^{-\alpha} + D_{1} |\Delta T|,$$  

where $2\beta \simeq 0.65$. This result clearly differs from the FT prediction, Eq. (4). In the mean-field approximation, the connection between complete scaling and the asymmetric Landau expansion has been investigated by Anisimov and Wang [23,24], who demonstrated that the two approaches appear to be consistent. Complete scaling has also been extended to inhomogeneous fluids by Bertrand and Anisimov [25]. That the penetrable-sphere model does not exhibit complete scaling has been investigated by Ren et al. [26], who found that this is due to a special symmetry of the model.

In addition to the leading $2\beta$ term in the excess density, complete scaling also predicts a divergence in the second derivative of the chemical potential along the coexistence curve

$$\left(\frac{d^2 \mu}{dT^2}\right)_{\text{cxc}} \sim |\Delta T|^{-\alpha},$$

where the subscript cxc denotes the conditions of phase coexistence. This so-called Yang-Yang anomaly derives its name from the Yang-Yang relation [27]

$$\frac{\rho C_V}{T} = \left(\frac{d^2 p}{dT^2}\right)_{\text{cxc}} - \rho \left(\frac{d^2 \mu}{dT^2}\right)_{\text{cxc}},$$

where $C_V$ is the isochoric heat capacity. Complete scaling implies the divergence of the isochoric heat capacity is shared between the second derivatives of the pressure and the chemical potential. In contrast, revised scaling predicts that $(d^2 \mu/dT^2)_{\text{cxc}}$ remains finite at the critical point. Nicol’s analysis also predicts nonanalytic behavior of the chemical potential, specifically,

$$\left(\frac{d^2 \mu}{dT^2}\right)_{\text{cxc}} \sim |\Delta T|^{-\alpha-\beta+\theta_5},$$

however, the relatively large value of $\theta_5$ ensures that this quantity remains finite at the critical point.

Fisher and co-workers have found support for complete scaling in heat-capacity measurements [28] and computer simulations of highly asymmetric fluid models [29–33]. However, heat-capacity measurements alone may not be sufficient evidence for complete scaling since small traces of impurities can mimic a Yang-Yang anomaly [34]. Anisimov and Wang have demonstrated that complete scaling is also supported by data on liquid-vapor coexistence in highly asymmetric fluids [23,24]. Some of the most compelling evidence for a $2\beta$ contribution has come from experiments near the critical consolute point in binary mixtures [35–40]. Several further investigations supporting the existence of a Yang-Yang anomaly have also recently been made [41,42]. There is also at least one model that exhibits the type of field mixing characteristic of complete scaling [43]. Complete scaling remains, however, an essentially phenomenological theory.

In this paper, we investigate the connection between complete scaling and the FT approach to asymmetric fluid criticality. After reviewing the thermodynamic implications of complete scaling in Sec. II, we develop a complete scaling equation of state in Sec. III. In Sec. IV, we extend the asymmetric LGW model and the resulting equation of state to systems that exhibit a Yang-Yang anomaly. The complete scaling and FT equations of state are systematically compared in Sec. V, with the finding that they are equivalent up to a term involving the higher-order asymmetric correction to scaling exponent $\theta_5$. Additionally, we investigate the possibility of extracting the complete scaling mixing parameters from a mean-field equation of state. In Sec. VI, we discuss implications of these results.

## II. COMPLETE SCALING

Critical phenomena of the Ising universality class are characterized by two independent scaling fields $h_1$ and $h_2$, known as the “ordering” and “thermal” fields, respectively, and a dependent scaling field $h_3(h_1,h_2)$, which serves as the thermodynamic potential. Asymptotically close to the critical point, the thermodynamic potential behaves as

$$h_3(h_1,h_2) \approx |h_2|^{2-\alpha|g|^{\frac{2}{1-\alpha-\beta}}} \left(\frac{h_1}{|h_2|^{\frac{2}{1-\alpha-\beta}}}ight),$$

where the superscript $\pm$ on the function $g$ distinguishes between $h_2 > 0$ ($+$) and $h_2 < 0$ ($-$). The critical point is defined by the condition $h_1 = h_3 = h_2 = 0$. The independent scaling fields are thermodynamically conjugate to two scaling densities $\phi_1$ and $\phi_2$, known as the “order parameter” and the “weakly fluctuating density,” respectively. The scaling fields and densities are connected by the thermodynamic relation

$$dh_3 = \phi_1 dh_1 + \phi_2 dh_2,$$

so that

$$\phi_1 = \left(\frac{\partial h_3}{\partial h_1}\right)_{h_2}, \quad \phi_2 = \left(\frac{\partial h_3}{\partial h_2}\right)_{h_1}.$$

The system exhibits stable two-phase equilibrium for $h_1 = 0$ and $h_2 < 0$. These two conditions define the Ising coexistence curve. Along the branches of the coexistence curve, the order parameter behaves asymptotically as

$$\phi_1 \approx \pm B|h_2|^\beta,$$

where the $\pm$ refers to the $h_1 > 0$ and $h_1 < 0$ sides of the coexistence curve, respectively. The weakly fluctuating density has the same value along both branches, namely,

$$\phi_2 \approx -\frac{A_0}{1-\alpha}|h_2|^{1-\alpha} + B_A|h_2|.$$
In these expressions, $A_0^-$ and $B_0$ are nonuniversal critical amplitudes. The term proportional to $B_+$ is an analytic fluctuation-induced contribution to $\phi_2$ [44]. For zero ordering field and positive $h_2$, the system is characterized by a single phase with $\phi_1 = 0$.

In one-component fluids, the thermodynamic fields are the temperature $T$, the chemical potential $\mu$, and the pressure $P$, and the conjugate densities are the number density $\rho$ and the entropy density $s$. The physical variables are interrelated by the Gibbs-Duhem relation

$$dP = \rho d\mu + s dT.$$  \hspace{1cm} (14)

Consequently, the densities are derived from the pressure as

$$\rho = \left(\frac{\partial P}{\partial \mu}\right)_T, \quad s = \left(\frac{\partial P}{\partial T}\right)_\mu.$$  \hspace{1cm} (15)

In addition to the reduced density $\Delta \rho$ and reduced temperature $\Delta T$,

$$\Delta \hat{\rho} = \frac{\rho - \rho_c}{\rho_c}, \quad \Delta \hat{T} = \frac{T - T_c}{T_c},$$  \hspace{1cm} (16)

it is convenient to define

$$\Delta \hat{s} = \frac{s - s_c}{\rho_c k_B}, \quad \Delta \hat{P} = \frac{P - P_c}{\rho_c k_B T_c}, \quad \Delta \hat{\mu} = \frac{\mu - \mu_c}{k_B T_c},$$  \hspace{1cm} (17)

where $k_B$ is Boltzmann’s constant.

For the liquid-vapor transition, the principle of complete scaling asserts that the scaling fields can be expanded in $\Delta \hat{\mu}, \Delta \hat{T},$ and $\Delta \hat{P}$. In the lowest order approximation, the scaling fields are given by

$$h_1 \simeq a_1 \Delta \hat{\mu} + a_2 \Delta \hat{T} + a_3 \Delta \hat{P},$$  \hspace{1cm} (18)

$$h_2 \simeq b_2 \Delta \hat{\mu} + b_3 \Delta \hat{P},$$  \hspace{1cm} (19)

$$h_3 \simeq c_1 \Delta \hat{P} + c_2 \Delta \hat{\mu} + c_3 \Delta \hat{T} + c_{23} \Delta \hat{\nu} \Delta \hat{T},$$  \hspace{1cm} (20)

where the constant coefficients are called mixing coefficients. In general, the complete scaling transformations should include terms of all orders in $\Delta \hat{T}, \Delta \hat{\mu},$ and $\Delta \hat{P}$. Consequently, some justifications of the truncated transformations presented above is required. In this work, we only consider contributions to the excess density $\Delta \hat{\nu}_j$ that are of order $|\Delta \hat{T}|^3$ or lower. Two second-order terms satisfy this criterion: $\Delta \hat{\nu} \Delta \hat{\mu}$ when added to $h_3$ and $\Delta \hat{T}^2$ when added to $h_1$ and $h_3$. However, we have omitted explicit $\Delta \hat{T}^2$ terms from the relations for $h_1$ and $h_3$ since these can be absorbed into the regular, i.e., noncritical, portion of the thermodynamic potential without affecting our results. The exact connection between the transformations, Eqs. (18)–(20), and the excess density will be derived in the following paragraphs. Once this connection is established, one can verify that the remaining second-order terms $\Delta \hat{\nu} \Delta \hat{\mu}, \Delta \hat{\nu} \Delta \hat{\mu},$ and $\Delta \hat{\nu}^2$ do not need to be included for our purposes.

As discussed by Wang and Anisimov [24] and Bertrand [45], the transformations, Eqs. (18)–(20), can be significantly simplified by selecting normalizations for the scaling fields, adopting a particular value of $\tilde{s} = s_c / \rho_c k_B$, which is arbitrary in classical thermodynamics, and neglecting higher-order terms. Specifically, we choose $\tilde{s} = (dP/dT)_{h_1 = 0}$, which can be implemented by adopting the following choice of coefficients:

$$a_1 = (1 - a), \quad a_2 = -a \tilde{s}, \quad a_3 = a,$$  \hspace{1cm} (21)

$$b_1 = 1, \quad b_2 = b, \quad b_3 = 0,$$  \hspace{1cm} (22)

$$c_1 = 1, \quad c_2 = -1, \quad c_3 = -\tilde{s}, \quad c_{23} = c.$$  \hspace{1cm} (23)

When these coefficients are substituted into the complete scaling transformations, we find, after defining for notational convenience

$$\Delta \tilde{P} = \Delta \hat{P} - \Delta \hat{\mu} - \tilde{s} \Delta \hat{T},$$  \hspace{1cm} (24)

that the transformations reduce to

$$h_1 = \Delta \hat{\mu} + a \Delta \tilde{P},$$  \hspace{1cm} (25)

$$h_2 = \Delta \hat{\mu} + b \Delta \tilde{P},$$  \hspace{1cm} (26)

$$h_3 = \Delta \tilde{P} + c \Delta \tilde{\nu} \Delta \hat{T}.$$  \hspace{1cm} (27)

In the mean-field approximation, $\Delta \hat{\mu} \sim |\Delta \hat{T}|^{3/2}$ and $\Delta \hat{P} \sim |\Delta \hat{T}|^2$, so that each asymmetric term in the complete scaling transformations is smaller than the leading term by a factor of $|\Delta \hat{T}|^{1/2}$. The revised scaling transformations are reproduced in the absence of pressure mixing ($a = 0$), and the lattice-gas model is recovered when all mixing coefficients are set to zero ($a = b = c = 0$).

The physical densities can be found in terms of the scaling densities by combining Eqs. (10), (14), and (25)–(27) with the result

$$\Delta \hat{\rho} = \frac{\phi_1 + b \phi_2 - c \Delta \hat{T}}{1 - a \phi_1},$$  \hspace{1cm} (28)

$$\Delta \hat{s} = \frac{\phi_2}{1 - a \phi_1},$$  \hspace{1cm} (29)

where $\phi_1$ and $\phi_2$ are given by Eqs. (12) and (13), respectively. To leading order in the asymmetry and reduced temperature, these expressions are given by

$$\Delta \hat{\rho} \simeq \phi_1 + a(\phi_2)^2 + b \phi_2 - c \Delta \hat{T},$$  \hspace{1cm} (30)

$$\Delta \hat{s} \simeq \phi_2.$$  \hspace{1cm} (31)

When the scaling densities presented in Eqs. (12) and (13) are substituted into Eq. (30), the complete scaling excess density introduced in Eq. (5) is reproduced with the coefficients

$$D_{2 \theta} = a(B_0)^2,$$  \hspace{1cm} (32)

$$D_{1-a} = -b \frac{A_0}{1 - a},$$  \hspace{1cm} (33)

$$D_1 = B_0 + c.$$  \hspace{1cm} (34)

We note that the leading $2\beta$ term is proportional to the pressure mixing coefficient $a$. The same is true of the Yang-Yang anomaly, which follows from the first complete scaling relationship [Eq. (25)] as

$$\left(\frac{d^2 \hat{\nu}}{d\hat{T}^2}\right)_{\text{exc}} \simeq -a \left(\frac{d^2 \hat{\rho}}{d\hat{T}^2}\right)_{\text{exc}} = -a A_0 |\Delta \hat{T}|^{-\alpha},$$  \hspace{1cm} (35)

where, to leading order, the coexistence curve is defined by $h_1 = 0$.

Complete scaling also predicts the effects of fluid asymmetry on other thermodynamic properties. In particular, the physical susceptibilities, such as the isothermal compressibility, volumetric expansivity, and the heat capacity are found
to be combinations of three scaling susceptibilities: “strong” $\chi_1 = (\partial \phi_1 / \partial h_1)_{h_2}$, “weak” $\chi_2 = (\partial \phi_2 / \partial h_2)_{h_1}$, and “cross” $\chi_3 = (\partial \phi_1 / \partial h_2)_{h_1}$ [24].

III. COMPLETE SCALING EQUATION OF STATE

The complete scaling transformations (25)–(27) are equivalent to an equation of state (EOS). In particular, these transformations describe the way in which an asymmetric EOS can be constructed from the symmetric Ising-type EOS, $h_3$. The third transformation, Eq. (27), when written as

$$\Delta \tilde{f}(\Delta \rho, \Delta T) = h_3(h_1, h_2) - c \Delta \mu \Delta \tilde{T},$$

is almost in the desired form, except that $h_3$ is a function of the scaling fields $h_1$ and $h_2$ and not the physical fields. The dependence of the potential $h_3$ on $\Delta \mu$ and $\Delta \tilde{T}$ can be made manifest by expanding in the asymmetric terms. If we define

$$h_3^{(0)}(\Delta \mu, \Delta \tilde{T}) = h_3(h_1) = \Delta \mu, h_2 = \Delta \tilde{T},$$

$$\phi_1^{(0)}(\Delta \mu, \Delta \tilde{T}) = \left( \frac{\partial h_3}{\partial h_1} \right)_{h_1=\Delta \mu, h_2=\Delta \tilde{T}},$$

then the double Taylor expansion of $h_3$ around $h_1 = \Delta \mu$ and $h_2 = \Delta \tilde{T}$ can be written as

$$h_3(h_1, h_2) \simeq h_3^{(0)} + \phi_1^{(0)}(a \Delta \tilde{P}) + \phi_2^{(0)}(b \Delta \mu).$$

We note that the functions $h_3^{(0)}$, $\phi_1^{(0)}$, and $\phi_2^{(0)}$ are the same functions as $h_3$, $\phi_1$, and $\phi_2$, as introduced in Eqs. (10) and (11). The superscript $(0)$ has been added to emphasize that these functions are now being evaluated at $(\Delta \mu, \Delta \tilde{T})$ instead of at the defined variables $(h_1, h_2)$. Equation (27) can now be written as

$$\Delta \tilde{P}(\Delta \mu, \Delta \tilde{T}) = \tilde{P}_\text{sym} + a \tilde{P}_a + b \tilde{P}_b + c \tilde{P}_c,$$

where

$$\tilde{P}_\text{sym}(\Delta \mu, \Delta \tilde{T}) = h_3^{(0)}(\Delta \mu, \Delta \tilde{T})$$

is the leading symmetric (lattice-gas) EOS and where the asymmetric corrections are given by

$$\tilde{P}_a(\Delta \mu, \Delta \tilde{T}) = \phi_1^{(0)}(\Delta \mu, \Delta \tilde{T}) h_3^{(0)}(\Delta \mu, \Delta \tilde{T}),$$

$$\tilde{P}_b(\Delta \mu, \Delta \tilde{T}) = \phi_2^{(0)}(\Delta \mu, \Delta \tilde{T}) \Delta \mu,$$

$$\tilde{P}_c(\Delta \mu, \Delta \tilde{T}) = -\Delta \mu \Delta \tilde{T}.$$
which is the leading symmetric (lattice-gas) Helmholtz energy, and where the asymmetric corrections are given by

\[ f^a_{cs}(\Delta \hat{\rho}, \Delta \hat{T}) = \Delta \hat{\rho} \psi^{(0)}(\Delta \hat{\rho}, \Delta \hat{T}) - \frac{1}{2} \Delta \hat{T}^2 \Delta \hat{\rho}^3 + \frac{u}{6} \Delta \hat{\rho}^3, \]

(58)

\[ f^b_{cs}(\Delta \hat{\rho}, \Delta \hat{T}) = -\phi^{(0)}_2(\Delta \hat{\rho}, \Delta \hat{T}) \psi^{(0)}_1(\Delta \hat{\rho}, \Delta \hat{T}), \]

(59)

\[ f^c_{cs}(\Delta \hat{\rho}, \Delta \hat{T}) = \Delta \hat{T} \psi^{(0)}_1(\Delta \hat{\rho}, \Delta \hat{T}). \]

(60)

We will refer to Eq. (56) as the complete scaling EOS. Expressions for \( f^a_{cs}, f^b_{cs}, \) and \( f^c_{cs} \), based on an \( \epsilon \)-expansion analysis of the symmetric LGW Hamiltonian, are given in the mean-field approximation in the following section and are presented to order \( \epsilon^2 \) in the Appendix. For practical applications, a parametric equation of state, such as the linear model [47], which has been shown to match the symmetric EOS [Eq. (57)] to order \( \epsilon^2 \) [48], may be used instead of the explicit \( \epsilon \) expansion.

Up until this point, nothing has prohibited us from including symmetric correction-to-scaling exponents and scaling functions in our definitions of the potential functions \( h_3 \) and \( \psi \) since we have treated the complete scaling transformations as a prescription that can be applied to any symmetric equation of state. In contrast, the forthcoming field-theoretic results hold only when the leading asymptotic terms are considered. Hence, we will now restrict \( f_{sym} \) to contain only the leading asymptotic terms and no higher-order Wegner corrections, so as to avoid confusion.

A. Complete scaling EOS in the mean-field approximation

In the mean-field approximation, which serves as an illustrative example for the concepts presented in this section, the complete scaling EOS takes on a particularly simple form. The asymptotic part of the symmetric Helmholtz energy is given by the following Landau expansion:

\[ E_{sym, mf} = \psi^{(0)}_{mf} = -\frac{1}{2} \Delta \hat{T}^2 \Delta \hat{\rho} - \frac{1}{2} \Delta \hat{T} \Delta \hat{\rho}^3 + \frac{u}{4!} \Delta \hat{\rho}^4, \]

(61)

where \( u \) is a constant. The corresponding ordering field and weakly fluctuating density are found from Eq. (48) to be

\[ h_{1, mf} = \Delta \hat{T} \Delta \hat{\rho} + \frac{u}{6} \Delta \hat{\rho}^3 \]

(62)

and

\[ \phi^{(0)}_{2, mf} = \frac{\Delta \hat{T}}{u} - \frac{1}{2} \Delta \hat{\rho}^2. \]

(63)

This last equation is the mean-field approximation of Eq. (13) with \( B_{\alpha \beta} = 0 \). The asymmetric contributions to the Helmholtz energy are found from the definitions given in Eqs. (58)–(60) to be

\[ f^a_{cs, mf} = -\frac{1}{2} \frac{\Delta \hat{T}^2}{u} \Delta \hat{\rho} - \frac{1}{2} \Delta \hat{T} \Delta \hat{\rho}^3 + \frac{u}{8} \Delta \hat{\rho}^5, \]

(64)

\[ f^b_{cs, mf} = -\frac{1}{2} \frac{\Delta \hat{T}^2}{u} \Delta \hat{\rho} + \frac{1}{5} \Delta \hat{T} \Delta \hat{\rho}^3 + \frac{u}{12} \Delta \hat{\rho}^5, \]

(65)

\[ f^c_{cs, mf} = (\Delta \hat{T})^2 \Delta \hat{\rho} + \frac{u}{6} (\Delta \hat{T} \Delta \hat{\rho}^3). \]

(66)

When these equations are substituted into Eq. (56), we find

\[ \Delta f_{cs, mf} = f_{sym, mf} + \left( cu - b - \frac{1}{2} a \right) \left( \Delta \hat{T}^2 \Delta \hat{\rho} - \frac{1}{2} \Delta \hat{T} \Delta \hat{\rho}^3 + \frac{u}{8} \Delta \hat{\rho}^5 \right) + \frac{1}{3!} (2b - 3a + cu) \Delta \hat{T} \Delta \hat{\rho}^5 \]

(67)

That the cubic term is proportional to the reduced temperature ensures that the EOS exhibits a critical point instead of a first-order transition.

IV. EXTENDED ASYMMETRIC LANDAU-GINZBURG-WILSON MODEL

Within a field-theoretic approach, Nicoll has analyzed the addition of asymmetric terms to the symmetric LGW Hamiltonian, such that the full Hamiltonian is of the form [16]

\[ \mathcal{H} = \mathcal{H}_{sym} + \mathcal{H}_{asym}, \]

(68)

where the symmetric Hamiltonian is given in terms of the spatially dependent field variable \( \phi(x) \) by

\[ \mathcal{H}_{sym} = \frac{1}{2} (\Delta \hat{T})^2 + \frac{1}{2} \Delta \hat{T} \Delta \hat{\rho}^3 + \frac{u}{4!} \Delta \hat{\rho}^4 - \frac{1}{2} \phi \nabla^2 \phi, \]

(69)

and where the asymmetric portion can be written as

\[ \mathcal{H}_{asym} = u_1 \phi_{1} + u_3 \phi_3 + u_5 \phi_5 + u_\alpha \phi_\alpha, \]

(70)

with

\[ O_1 = \frac{1}{2} (\Delta \hat{T})^2 \phi, \quad O_3 = \frac{1}{2!} (\Delta \hat{T})^3 \phi_3, \]

(71)

\[ O_5 = \frac{u}{3!} \phi^5, \quad O_\alpha = -\frac{1}{3!} \phi \nabla^2 \phi \phi_\alpha. \]

(72)

We will refer to the \( u_i \) as asymmetry coefficients. We note that \( \mathcal{H}_{sym} \) is symmetric under the transformation \( \phi \rightarrow -\phi \), whereas \( \mathcal{H}_{asym} \) is antisymmetric. In terms of the ordering field \( h_1 \), the Hamiltonian is related to the pressure \( \Delta \tilde{P} = \Delta P(h_1, \Delta \hat{T}) \) by the following functional integral:

\[ \Delta \tilde{P} = \ln \left\{ \int D\phi \exp \left[ \int dx (\phi h_1 - \mathcal{H}) \right] \right\}. \]

(73)

The phase boundary is described by \( h_1 = 0 \), at least in the symmetric case and to leading order in the asymmetric case. The field-theoretic treatment itself does not provide any immediate guidance for specifying the relationship between \( h_1 \) and the physical fields. Both \( h_1 = \Delta \hat{\mu} - \Delta \hat{\mu}_{cxc}(T) \) and \( h_1 = \Delta \tilde{P} - \Delta P_{cxc}(T) \) or a combination of the two appear to be satisfactory, where the subscript cxc denotes the conditions of phase coexistence. However, the ordering field can not be a singular function of the temperature, so not every choice is acceptable. In particular, the relationship between \( h_1 \) and the physical fields should differ depending on whether or not the system exhibits a Yang-Yang anomaly, i.e., \( d^2 \mu_{cxc}/dT^2 \sim |\Delta \hat{T}|^\alpha \). If \( \mu_{cxc}(T) \) is analytic, i.e., no Yang-Yang anomaly, the ordering field can be taken as

\[ h_1 = \Delta \hat{\mu} - \Delta \hat{\mu}_{cxc}(T). \]

(74)
A term proportional to \( \Delta \hat{P} - \Delta \hat{P}_{\text{xc}}(T) \), i.e., pressure mixing, can not be included since \( \Delta \hat{P}_{\text{xc}}(T) \) is not analytic in \( T \). In this case, as discussed below Eq. (20), the term \( \Delta \mu_{\text{xc}}(T) \) can be absorbed into the regular part of the thermodynamic potential leaving
\[
h_1 = \Delta \hat{\mu},
\]
which is the definition of the ordering field for both the lattice gas \( (a = b = c = 0) \) and revised scaling \( (a = 0) \). As seen from Eq. (73), \( h_1 \) is thermodynamically conjugate to \( \langle \varphi \rangle \), where the brackets denote an ensemble average. Therefore, \( \langle \varphi \rangle = \Delta \hat{\mu} \) in the absence of a Yang-Yang anomaly.

In contrast, when \( \mu_{\text{xc}}(T) \) is nonanalytic in \( T \) at the critical point, Eq. (74) is no longer valid. Instead, the pressure is “mixed” into \( h_1 \) as
\[
h_1 = [\Delta \hat{\mu} - \Delta \mu_{\text{xc}}(T)] + a[\Delta \hat{P} - \Delta \hat{P}_{\text{xc}}(T)],
\]
where the value of \( a \) is selected to ensure the analyticity of \( h_1 \). This leads to the complete scaling relation for the ordering field [cf. Eq. (25)] since for our choice of \( \tilde{\xi} \), \( \Delta \tilde{\mu}_{\text{xc}}(T) \approx -a \Delta \tilde{P}_{\text{xc}}(T) \). The pressure mixing ensures the analyticity of \( h_1 \) when \( \tilde{\mu}_{\text{xc}}(T) \) is nonanalytic. By taking a functional derivative of Eq. (73) with respect to \( h_1 \), we find that
\[
\langle \varphi \rangle \simeq \Delta \hat{\rho} - a(\Delta \hat{\rho})^2.
\]

The relationship between the Helmholtz energy \( \Delta \tilde{f} = \Delta \tilde{f}(\langle \varphi \rangle, \Delta \tilde{T}) \), and the Hamiltonian is found by applying a Legendre transformation, Eqs. (51), to (73), with the result
\[
\Delta \tilde{f} = -\ln \left\{ \int \mathcal{D} \varphi \exp \left[ \int d\varphi (\varphi h_1 - \Delta \hat{\mu} \Delta \hat{\rho} - h_1 \varphi) \right] \right\}.
\]

This integral can be evaluated perturbatively in the loop expansion [49]. To linear order in the asymmetry, each operator \( O_I \) in \( \mathcal{H} \) produces a distinct contribution \( f_I^{\text{FT}} \) to the total Helmholtz energy, which may now be written as
\[
\Delta \tilde{f} = f_{\text{sym}}(\langle \varphi \rangle, \Delta \tilde{T}) + \Delta \hat{\mu} \Delta \hat{\rho} - h_1 \langle \varphi \rangle \nonumber + u_1 f_1^{\text{FT}} + u_3 f_3^{\text{FT}} + u_5 f_5^{\text{FT}} + u_7 f_7^{\text{FT}},
\]
where the asymmetry coefficients \( u_i \) were introduced in the definition of the asymmetric LGW Hamiltonian (70). We note that \( f_{\text{sym}} \) in this expression only includes the leading asymmetric portion of the symmetric Helmholtz energy and does not include any symmetric correction-to-scaling terms. The above result can now be expanded to linear order in \( a \), which produces
\[
\Delta \tilde{f}_{\text{FT}}(\Delta \hat{\rho}, \Delta \tilde{T}) = f_{\text{sym}} + a f_a^{\text{CS}} + u_1 f_1^{\text{FT}} + u_3 f_3^{\text{FT}} + u_5 f_5^{\text{FT}} + u_7 f_7^{\text{FT}},
\]
where \( f_a^{\text{CS}} \) is given by Eq. (58) and where the subscript FT has been used to differentiate this Helmholtz energy from the complete scaling EOS, Eq. (56). We will refer to this as the FT EOS. Expressions for \( f_1^{\text{FT}}, f_3^{\text{FT}}, \) and \( f_5^{\text{FT}} \) are given in the mean-field approximation in the following section and are presented to order \( \epsilon^2 \) in the Appendix.

### A. FT EOS in the mean-field approximation

In the mean-field approximation, the \( f_I^{\text{FT}} \) are given by
\[
f_{1,\text{mf}}^{\text{FT}} = (\Delta \tilde{T})^2 \frac{\Delta \hat{\rho}}{u}, \quad f_{3,\text{mf}}^{\text{FT}} = \frac{1}{3!} (\Delta \tilde{T}) \Delta \hat{\rho}^3, \quad f_{5,\text{mf}}^{\text{FT}} = \frac{u}{5!} \Delta \hat{\rho}^5, \quad f_{7,\text{mf}}^{\text{FT}} = 0.
\]

The asymmetric gradient operator \( O_3 \) does not contribute at the mean-field level for a homogeneous system \( (\nabla \hat{\rho} = 0) \), but does affect inhomogeneous systems [25]. When these results are combined with Eq. (80) for the FT EOS, the resulting Helmholtz energy is given by the asymmetric Landau expansion
\[
\Delta \tilde{f}_{\text{FT},\text{mf}} = f_{\text{sym},\text{mf}} + \left( u_1 - \frac{1}{2} a \right) \frac{(\Delta \tilde{T})^2}{u} \Delta \hat{\rho} \nonumber + \frac{1}{3!} (u_3 - 3a) (\Delta \tilde{T}) \Delta \hat{\rho}^3 + \frac{u}{5!} (u_5 - 15a) \Delta \hat{\rho}^5,
\]
where \( f_{\text{sym},\text{mf}} \) is given by Eq. (61). Generally, when a Taylor expansion of a mean-field EOS, such as the van der Waals EOS, is made around the critical point \( (\rho_c, T_c) \), the result is expressed with only a single coefficient for each term, for example,
\[
\Delta \tilde{f}_{\text{mf}} = f_{\text{sym},\text{mf}} + k_1 \frac{(\Delta \tilde{T})^2}{u} \Delta \hat{\rho} \nonumber + \frac{1}{3!} k_3 (\Delta \tilde{T}) \Delta \hat{\rho}^3 + \frac{u}{5!} k_5 \Delta \hat{\rho}^5.
\]

Hence, if the expansion coefficients are known, these should be associated with \( k_1, k_3, k_5 \), and not the asymmetry coefficients from the asymmetric LGW Hamiltonian (70) since they differ by terms proportional to the mixing coefficient \( a \). Of course, the two are related by
\[
k_1 = u_1 - \frac{1}{2} a, \quad k_3 = u_3 - 3a, \quad k_5 = u_5 - 15a.
\]

### V. COMPARISON OF THE COMPLETE SCALING
AND FT EQUATIONS OF STATE

We are now in a position to ascertain the nature of the relationship between the complete scaling and FT equations of state, given by Eqs. (56) and (80), respectively. First, we note that, in the context of the \( \epsilon \) expansion, \( f_1^{\text{FT}} \) is proportional to \( f_{1,\text{mf}}^{\text{FT}} \). Therefore, \( f_1^{\text{FT}} \) produces a contribution to \( \Delta \hat{\mu} \) proportional to \( \Delta \hat{T}^2 \). As discussed in the text below Eq. (20), this type of term can be incorporated via field mixing or absorbed into the regular part of the thermodynamic potential. Consequently, we will treat the asymmetry coefficient \( u_1 \) as a free parameter, with the knowledge that the regular part of the thermodynamic potential should be modified accordingly. Two of the asymmetric contributions to the CS EOS [Eq. (56)], \( f_b^{\text{CS}} \) and \( f_c^{\text{CS}} \), which are expressed in terms of the symmetric functions \( h_1 \) and \( \varphi \) in Eqs. (59) and (60), can also be expressed in terms of \( f_1^{\text{FT}}, f_3^{\text{FT}}, f_5^{\text{FT}}, \) and \( f_7^{\text{FT}} \) as derived from the...
asymmetric LGW Hamiltonian and introduced in Eq. (79). Specifically, one has
\[
\begin{align*}
\tilde{f}_{CS} & = uf_1^{FT} + f_3^{FT}, \\
\tilde{f}_{b}^{CS} & = -f_1^{FT} + 2f_3^{FT} + 10f_5^{FT} + 3f_5^{FT}.
\end{align*}
\] (88)

These equalities can be verified in the mean-field approximation by combining Eqs. (64)–(66), (81) and (82), and to order \(\epsilon^2\) using the results given in the Appendix. The simplicity of the expression for \(\tilde{f}_{CS}^{CS}\) stems from the fact that the cubic operator \(O_3\) can effectively be removed from the Hamiltonian, without altering other terms at leading order, by transforming the field variable as \(\psi \rightarrow \psi - (u_3/a)\Delta T\). This simply leads to a shift proportional to \(\Delta T\) in the order parameter \(\langle \psi \rangle\). Interestingly, Eqs. (88) and (89) are quite general and can be proven outside the context of the \(\epsilon\) expansion [16]. Like \(\tilde{f}_{CS}^{CS}\) and \(\tilde{f}_{CS}^{FT}\), the pressure-mixing term \(\tilde{f}_{b}^{CS}\) can be expressed as a linear combination of \(f_1^{FT}, f_3^{FT}, f_5^{FT}\), and \(f_7^{FT}\) through order \(\epsilon\) [45]. However, this type of relationship breaks down for \(\tilde{f}_{CS}^{CS}\) at order \(\epsilon^2\).

Equations (88) and (89) for \(\tilde{f}_{CS}^{CS}\) and \(\tilde{f}_{CS}^{FT}\) allow us to rewrite the FT EOS, Eq. (80), as
\[
\Delta f_{FT}^{CS} = f_{sym} + a f_{CS}^{CS} + b f_{CS}^{FT} + c f_{e} + u_s^{eff} f_5,
\] (90)
where
\[
\begin{align*}
cu & = u_3 - (2/3)u_5, \\
b & = (1/3)u_5, \\
u_s^{eff} & = u_5 - \frac{10}{3}u_5.
\end{align*}
\] (91–93)

The term proportional to \(u_s^{eff}\) is responsible for the asymmetric correction-to-scaling exponent \(\theta_5\) introduced in Eq. (4). In particular, in Eq. (4), \(D_{\theta + \theta_5}\) is proportional to \(u_s^{eff}\) [16]. The relationship between the FT EOS [Eq. (80)] and the complete scaling EOS [Eq. (56)] can be compactly written as
\[
\Delta f_{FT} = \Delta f_{CS} + u_s^{eff} f_5^{FT},
\] (94)
and the corresponding excess density can be written as
\[
\Delta \rho_{s} \approx D_{1 - u} |\Delta T|^{1 + \epsilon} + D_{2b} |\Delta T|^{2\beta} + D_{1}|\Delta T| + D_{\beta + \theta_5}|\Delta T|^{\beta + \theta_5},
\] (95)
where the coefficients and exponents are the same as those introduced in Sec. I. We note that the above expression matches that proposed by Fisher and co-workers [21] if one omits the symmetric Wegner correction as we have. The implementation of complete scaling as defined by Eqs. (25)–(27) assumes that all leading sources of asymmetry can be mapped onto a symmetric EOS through the mixing of fields. Equation (94) quantifies the extent to which this assumption holds. Clearly, the term proportional to \(u_s^{eff}\) prohibits an exact mapping. This reflects the fact that \(\theta_5\) is an independent critical exponent and cannot be expressed in terms of Ising exponents. However, since the \(\theta_5\) contribution to thermodynamic properties is significantly higher order in the scaling regime than the lowest-order mean-field contribution, the term proportional to \(u_s^{eff}\) can not likely be resolved in practical applications. However, as highlighted in the following paragraph, some care is required in omitting this term because it may compromise the thermodynamic consistency of the theory.

A. Comparison of the complete scaling and FT equations of state in the mean-field approximation

The mean-field approximation of Eq. (94) reads as
\[
\Delta f_{FT, mf} = \Delta f_{CS, mf} + u_s^{eff} \frac{u}{5!} \Delta \rho^{5},
\] (96)
where \(\Delta f_{FT, mf}\) and \(\Delta f_{CS, mf}\) are given by Eqs. (83) and (67), respectively. As previously noted, the term proportional to \(u_s^{eff}\) breaks the full isomorphism between the symmetric and asymmetric Helmholtz energies. In the mean-field approximation, the \(\theta_5\) contribution stemming from this term is of the same order as the other leading asymmetric terms, e.g., \(|\Delta T|^{\theta + \theta_5}\) is proportional to \(|\Delta T|\) in the excess density, and therefore it can not be consistently neglected, as was the case in the scaling regime. To emphasize the above point, we consider the van der Waals EOS. For this EOS, the Landau expansion has \(k_3 = k_5 = 0\) [24], where \(k_1\) and \(k_3\) were introduced in Eq. (84). These coefficients are consistently represented by \(a = u_1 = u_3 = 0\), hence,
\[
\Delta f_{vdw, mf} = f_{sym, mf} + u_s^{eff} \frac{u}{5!} \Delta \rho^{5},
\] (97)
where \(f_{sym, mf}\) is given by Eq. (61). As a consequence, all asymmetry in the van der Waals excess density comes entirely from the \(|\Delta T|^{\theta + \theta_5}\) term. If \(u_s^{eff}\) were simply neglected for the van der Waals EOS, which would imply that complete scaling as formulated in Sec. II is exact, one instead finds nonzero values of \(a, b,\) and \(c\). However, these values would not have a thermodynamically consistent connection to the scaling regime.

It seems physically plausible for a simple intermolecular potential, such as the Lennard-Jones potential, that the coefficient in front of the asymmetric gradient term \(u_5\) could be proportional to \(u_s\), the coefficient that defines the asymmetry of the mean-field EOS. If this is the case and the constant of proportionality is known, all of the complete scaling mixing parameters could be extracted from a mean-field EOS. This possibility leads us to consider the particularly interesting case of an exact isomorphism between the symmetric and asymmetric equations of state characterized by \(u_s^{eff} = u_5 - (10/3)u_5 = 0\). For this case, there is a special relationship between the complete scaling mixing parameters and the mean-field expansion coefficients introduced in Eq. (84):
\[
\begin{align*}
k_1 & = cu - b - \frac{1}{2}a, \\
k_3 & = 2b - 3a + cu, \\
k_5 & = 10b - 15a,
\end{align*}
\] (98–100)
which can be found by combining Eqs. (67) and (84). These relationships can be inverted to yield expressions for the mixing coefficients in terms of the Hamiltonian coefficients. As an example, if we return to the case of the van der Waals EOS, we find
\[
\begin{align*}a & = \frac{1}{3}k_5, \\
b & = \frac{1}{6}k_5, \\
cu & = \frac{1}{2}k_5.
\end{align*}
\] (101–103)
As noted earlier, the value of \( u_1 \) does not affect the physical quantities of interest. If for convenience we take \( u_1 = 0 \), which implies that \( k_1 = -1/2\epsilon \), then \( cu = b \) and we are left with the mean-field relations of Wang and Anisimov [24]:

\[
\begin{align*}
    a &= \frac{3}{2}k_3 - \frac{1}{2}k_5, \\
    b &= k_3 - \frac{1}{2}k_5,
\end{align*}
\]

(104, 105)

who omitted the nonlinear mixing contribution \( \Delta \mu \Delta T \) from their analysis and implicitly set \( u_5^{\text{eff}} = 0 \).

VI. CONCLUSION AND DISCUSSION

In this work, we have established the nature of relationship between complete scaling and the FT approach to asymmetric fluid criticality. In Eqs. (25)–(27), complete scaling transformations were presented in a particularly succinct form, which emphasizes the connection between the leading asymmetric corrections to thermodynamic properties and the leading asymmetric corrections to each scaling field. These transformations were used to define the complete scaling equation of state presented in Eq. (56). The previous treatment of the asymmetric LGW Hamiltonian was extended to systems that exhibit a Yang-Yang anomaly in Sec. IV and the resulting “FT” equation of state was given in Eq. (80). It was argued that pressure mixing is required to ensure the analyticity of the ordering field when the chemical potential along the coexistence curve is nonanalytic. The complete scaling and FT equations of state are nearly identical, except that the FT equation of state has an additional term responsible for the asymmetric correction-to-scaling exponent \( \theta_5 \). The relationship between the two equations of state is compactly summarized by Eq. (94). For many practical applications, the contribution from \( \theta_5 \) can be neglected. In this regime, the complete scaling and FT approaches are equivalent. However, as emphasized in Sec. V, care is required in applying this simplification to the mean-field approximation because the terms involving \( \theta_5 \) are the same order as the other leading asymmetric corrections.

There is an analogy between the asymmetric correction-to-scaling exponent \( \theta_3 \) and the Wegner correction-to-scaling exponent \( \Delta \simeq \epsilon/2 \) [50]. The Wegner correction arises from the difference between the renormalization-group fixed-point coupling constant \( u^* \) and the system-dependent mean-field value of the coupling constant \( u \). When the Wegner correction is included, the Ising field-dependent potential [cf. Eq. (9)] reads as [51]

\[
h_{3,\text{sym}} \approx |h_2|^{2-a} g^\pm(\epsilon)[1 + |h_2|^{\Delta} g^\pm(\epsilon)],
\]

(106)

where \( \epsilon = h_1/|h_2|^{2-a-\beta} \) and \( g^\pm \propto (u^* - u) \). The connection between the FT EOS and the complete scaling EOS expressed through Eq. (94) suggests that FT EOS, Eq. (80), which omits the Wegner correction, can be written in a similar form as

\[
h_3 \approx |h_2|^{2-a} g^\pm(\epsilon)[1 + |h_2|^{\Delta} g^\pm(\epsilon)],
\]

(107)

where \( g^\pm \propto u_5^{\text{eff}} = u_5 - (10/3)u_2 \). As in the case of the Wegner correction, which is associated with an additional critical amplitude \( u^* - u \), the \( \theta_5 \) exponent is associated with the new critical amplitude \( u_5^{\text{eff}} \). We note that if \( u_5 = (10/3)u_2 \), \( h_3 \) includes only the leading asymptotic terms, and complete scaling becomes exact. The similarity between Eqs. (106) and (107) suggests that the FT EOS could be extended to include the Wegner correction by writing it as

\[
h_3 \approx |h_2|^{2-a} g^\pm(\epsilon)[1 + |h_2|^{\Delta} g^\pm(\epsilon)] + |h_2|^{\theta_5} g^\pm(\epsilon).
\]

(108)

However, there is a significant difference between these two corrections to scaling. Unlike \( \theta_3 \), the exponent \( \Delta \) vanishes in the mean-field approximation \( \epsilon = 0 \). This explains why the Wegner correction can be consistently omitted in the mean-field approximation. The same is not true for \( \theta_5 \) because in the mean-field approximation \( \theta_5 = 1/2 \).

An apparent ambiguity in the physical definition of the order parameter is found for liquid-liquid mixtures, where the number of physical densities, e.g., mole fraction, volume fraction, mass fraction, is greater than in the liquid-vapor case [40]. As shown by Wang et al. [36], the dilemma of defining the correct complete scaling order parameter is explicit for incompressible binary mixtures. With an isomorphic choice of coefficients, the density \( \hat{\rho} \), mole fraction \( x \), and partial molar density \( \hat{\rho} x \) are given by

\[
\begin{align*}
\hat{\rho} &= 1 + a \phi_1, \\
\rho &= x_0 + (1-a) \phi_1 + b \phi_2, \\
\hat{\rho} x &= x_0 + (1-a) \phi_1 + b \phi_2,
\end{align*}
\]

(109, 110, 111)

where, along the coexistence curve, \( \phi_1 \) and \( \phi_2 \) are given by Eqs. (12) and (13). Complete scaling predicts a \( 2\beta \) term for the mole fraction but not for either the total density or the partial molar density. This implies that, in translating the results of this work to incompressible binary mixtures, the fluctuating field \( \phi \) in Sec. IV should be connected to the mole fraction \( x \) by

\[
\langle \phi \rangle = \hat{x} - a \hat{x}^2.
\]

(112)

As discussed by Bertrand and Anisimov [25], the asymmetric-gradient coefficient \( u_3 \) also contributes to the asymmetry of the correlation length \( \xi \) via

\[
\xi^2 \simeq (\xi_{\text{sym}})^2 [1 + (3a + u_3) \beta_0 |\Delta \hat{T}|^{\beta}],
\]

(113)

where the piece proportional to \( a \) originates from asymmetry in the physical susceptibility \( (\partial \rho/\partial \mu)/T \). By measuring the physical susceptibility and the correlation length in both the upper (lighter) and the lower (denser) coexisting fluid phases by light scattering, one can obtain \( a \) and \( u_3 \) independently. These values could be compared to those obtained from excess density data to conclusively determine the extent to which neglecting \( u_5^{\text{eff}} \) is a good approximation.

In the mean-field approximation, the isochoric heat capacity does not diverge at the critical point, but instead exhibits a jump discontinuity along the critical isochore. In the scaling regime, this discontinuity develops into a critical point singularized characterized by the exponent \( -\alpha \). Similarly, \( d^2 \mu_{\text{exc}}/dT^2 \) exhibits a jump discontinuity in the mean-field approximation, for instance, for the van der Waals EOS. However, unlike the case of the heat capacity, a field-theoretic treatment of the asymmetric LGW Hamiltonian (70) does not predict whether or not this discontinuity develops into a singularity or vanishes in the scaling regime. Instead, it appears, as discussed in...
Sec. IV, that the interpretation of the FT results can only be modified through an appropriate assignment of \( h_{1} \) to accommodate, but not predict, a singularity in the second temperature derivative of the chemical potential along the coexistence curve. The results presented in Sec. V shed light on this issue in the calculation of the FT analysis of the asymmetric LGW Hamiltonian. Just like the work of Wang and Anisimov [24], the results presented in [52] are only applicable to the specific cases of the critical molecular volume to the interaction volume, as determined by the correlation length, observed for the liquid-vapor transition [24] and similar correlations between the analogous mixing coefficient and the ratio of molecular volumes observed in nitrobenzene and \( n \)-alkane mixtures [36].

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### APPENDIX: ORDER \( \epsilon^{2} \) RESULTS

In this Appendix, we give expressions to order \( \epsilon^{2} \), in the \( \epsilon \) expansion, where \( \epsilon = 4 - d \) and \( d \) is the spatial dimensionality, for \( f_{a}^{CS} \), \( f_{b}^{CS} \), and \( f_{c}^{CS} \) as defined by Eqs. (58)–(60), and for \( f_{a}^{FT} \) , \( f_{b}^{FT} \), and \( f_{c}^{FT} \), which were introduced in Eq. (79). The \( \epsilon \) expansion yields results for the critical exponents and the Ising EOS that are significantly more accurate than those of the mean-field approximation used in Secs. III–V [49]. While many of the results contained in this Appendix have been presented elsewhere [16], we present them here for completeness and to ensure notational consistency. In the text, we stated that Eqs. (88) and (89) hold to order \( \epsilon^{2} \). In this appendix, we provide the material necessary to verify this statement.

To order \( \epsilon^{2} \), the symmetric Helmholtz energy based on the \( \epsilon \) expansion of the symmetric LGW Hamiltonian (69) is given by

\[
\psi(\Delta \tilde{\rho}, \Delta \tilde{T}) = \psi_{\text{mf}}^{(0)} - \frac{1}{2} \kappa \tilde{\rho}^{2} \left[ \frac{\kappa - \epsilon}{1 - \epsilon} - B_{0} \right] + \frac{u}{8} \kappa^{2} (L + 1)^{2} + \frac{u^{2}}{8} \Delta \tilde{\rho}^{2} (L^{2} - f),
\]

where, by definition,

\[
\kappa^{2} = \Delta \tilde{T} + \frac{u}{2} \Delta \tilde{\rho}^{2},
\]

\( L = \ln(\kappa^{2}), \ f = 4 + \pi^{2} + 8\lambda (\lambda \approx 1.17), \ B_{0} = 1 + \epsilon/2, \) and where \( \psi_{\text{mf}}^{(0)} \) is given by Eq. (61). Combining the above expression for \( \delta \psi \) with the definitions of \( h_{1} \) and \( \phi_{2} \) furnished by Eq. (48), one finds that

\[
\begin{align*}
\phi_{2}(\Delta \tilde{\rho}, \Delta \tilde{T}) &= \phi_{2,\text{mf}}^{(0)} + \frac{\kappa^{2}}{\epsilon} [\kappa - \epsilon - B_{0}] \\
&+ \frac{u^{2}}{4} \kappa^{2} \Delta \tilde{\rho}^{2} (L + 1)(L + 2) + L^{2} - f \\
&+ \frac{u}{8} \Delta \tilde{\rho}^{3} (L^{2} - f + 2L)
\end{align*}
\]

and

\[
\phi_{2}(\Delta \tilde{\rho}, \Delta \tilde{T}) = \phi_{2,\text{mf}}^{(0)} + \frac{\kappa^{2}}{\epsilon} [\kappa - \epsilon - B_{0}] \\
- \frac{u}{4} \kappa^{2} (L + 1)(L + 2) - \frac{u^{2}}{8} \Delta \tilde{\rho}^{2} (L^{2} - f + 2L),
\]

where \( h_{1,\text{mf}}^{(0)} \) and \( \phi_{2,\text{mf}}^{(0)} \) are given by Eqs. (62) and (63), respectively. For the following, it is helpful to define

\[
\begin{align*}
\delta h_{1}(\Delta \tilde{\rho}, \Delta \tilde{T}) &= h_{1}(\Delta \tilde{\rho}, \Delta \tilde{T}) - h_{1,\text{mf}}^{(0)}(\Delta \tilde{\rho}, \Delta \tilde{T}) \\
\delta \psi(\Delta \tilde{\rho}, \Delta \tilde{T}) &= \psi(\Delta \tilde{\rho}, \Delta \tilde{T}) - \psi_{\text{mf}}^{(0)}(\Delta \tilde{\rho}, \Delta \tilde{T}).
\end{align*}
\]

The pieces of the complete scaling Helmholtz energy, \( f_{a}^{CS} \), \( f_{b}^{CS} \), and \( f_{c}^{CS} \), can be calculated to order \( \epsilon^{2} \) through Eqs. (58)–(60), with the following results:

\[
\begin{align*}
 f_{a}^{CS}(\Delta \tilde{\rho}, \Delta \tilde{T}) &= f_{a,\text{mf}}^{CS} + (\Delta \tilde{\rho}) \delta \psi(\Delta \tilde{\rho}, \Delta \tilde{T}) \\
&- (\Delta \tilde{\rho})^{2} \delta h_{1}(\Delta \tilde{\rho}, \Delta \tilde{T}),
\end{align*}
\]

\[
 f_{b}^{CS}(\Delta \tilde{\rho}, \Delta \tilde{T}) = f_{b,\text{mf}}^{CS} + 2 \frac{\Delta \tilde{\rho}^{2}}{3} \delta h_{1}(\Delta \tilde{\rho}, \Delta \tilde{T}) \\
+ \frac{u}{4} \Delta \tilde{\rho} \kappa^{2} [(L + 1)^{2} + \left( \frac{u}{3} \Delta \tilde{\rho}^{2} - \kappa^{2} \right)(L^{2} - f)],
\]

\[
 f_{c}^{CS}(\Delta \tilde{\rho}, \Delta \tilde{T}) = f_{c,\text{mf}}^{CS} + (\Delta \tilde{T}) \delta h_{1}(\Delta \tilde{\rho}, \Delta \tilde{T}),
\]

where \( f_{a,\text{mf}}^{CS}, f_{b,\text{mf}}^{CS}, \) and \( f_{c,\text{mf}}^{CS} \) are given by Eqs. (64)–(66). The expressions, resulting from an \( \epsilon \)–expansion analysis of the asymmetric LGW Hamiltonian (70), for the asymmetric contributions to the Helmholtz energy in Eq. (79) are

\[
\begin{align*}
f_{a}^{FT}(\Delta \tilde{\rho}, \Delta \tilde{T}) &= f_{a,\text{mf}}^{FT} + \frac{1}{6} \Delta \tilde{\rho}^{3} \delta h_{1}(\Delta \tilde{\rho}, \Delta \tilde{T}) \\
&+ \frac{u}{8} \kappa^{2} \Delta \tilde{\rho}^{2} \left[ \kappa^{2}(L + 1)^{2} + \frac{u^{2}}{3} \Delta \tilde{\rho}^{2}(L^{2} - f) \right].
\end{align*}
\]
\[
\begin{aligned}
&f^\text{FT}_3(\Delta \rho, \Delta \tilde{T}) = f^\text{FT}_{3,\text{int}} + \frac{\Delta \tilde{T}}{u} \delta h_1(\Delta \rho, \Delta \tilde{T}), \\
&f^\text{FT}_\lambda(\Delta \rho, \Delta \tilde{T}) = 7f^\text{FT}_{3,\text{int}} - \frac{2\kappa^2}{3u} \delta h(\Delta \rho, \Delta \tilde{T}) - \frac{u}{6} \kappa^2 \Delta \tilde{T} \left\{ \frac{3}{2} u \Delta \tilde{T} (L^2 - f) + \kappa^2 \left[ 2(L + 1)^2 + \frac{1}{2} L^2 - f \right] \right\},
\end{aligned}
\]  

(11)

and

(12)

where \(f^\text{FT}_{3,\text{int}}, f^\text{FT}_{3,\text{int}}\), and \(f^\text{FT}_{\lambda}\) are given by Eqs. (81) and (82). The relationships between \(f^\text{CS}, f^\text{CS}_c\), and \(f^\text{FT}_3, f^\text{FT}_\lambda\), and \(f^\text{FT}_\lambda\), given by Eqs. (88) and (89), can now be readily verified to order \(\epsilon^2\) with the expression presented in this Appendix.