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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, $\Delta\hat{\rho} = (\rho - \rho_c)/\rho_c$, where ρ_c is the value of the number (molar) density at the critical point. 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

$$\Delta\hat{\rho}_d = \frac{\Delta\hat{\rho}^+ + \Delta\hat{\rho}^-}{2}. \quad (1)$$

For the lattice gas $\Delta\hat{\rho}_d = 0$. However, real fluids do not possess the symmetry of the Ising model, and in general

$\Delta\hat{\rho}_d \neq 0$. Even the coexistence curve of ³He, 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 sub-leading 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]

$$\Delta\hat{\rho}_d = D_1|\Delta\hat{T}|, \quad (2)$$

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, like SF₆ [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 non-classical, *i.e.*, non-mean-field, behavior of the excess density. On the basis of these models, a non-classical 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 μ and temperature T , whereas the lattice gas model assumes that μ and T are the correct scaling fields. This field mixing produces the following asymptotic behavior:

$$\Delta\hat{\rho}_d \approx D_{1-\alpha}|\Delta\hat{T}|^{1-\alpha} + D_1|\Delta\hat{T}|, \quad (3)$$

where $\alpha \simeq 0.11$ [14] ($1 - \alpha \simeq 0.89$) 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

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found that these asymmetric operators also lead to a non-analytic correction to the excess density characterized by a new asymmetric correction-to-scaling exponent θ_5 . The excess density predicted by their analysis goes as

$$\Delta\hat{\rho}_d \approx D_{1-\alpha}|\Delta\hat{T}|^{1-\alpha} + D_1|\Delta\hat{T}| + D_{\beta+\theta_5}|\Delta\hat{T}|^{\beta+\theta_5}, \quad (4)$$

where $\beta \simeq 0.326$ [14]. The universal exponent θ_5 was found to be $\theta_5 = 1/2 + \epsilon = 3/2$ in the first-order ϵ -expansion, where $\epsilon = 4 - d$ and d is the spatial dimensionality [17, 18]. Working to order ϵ^3 , Zhang and Zia [19], found their results to be consistent with the bound $\theta_5 \gtrsim 1.0$.

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 μ , 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

$$\Delta\hat{\rho}_d \approx D_{2\beta}|\Delta\hat{T}|^{2\beta} + D_{1-\alpha}|\Delta\hat{T}|^{1-\alpha} + D_1|\Delta\hat{T}|, \quad (5)$$

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 2β term in the excess density, complete scaling also predicts a divergence in the second derivative of the chemical potential along the coexistence curve

$$\left(\frac{d^2\mu}{dT^2}\right)_{\text{cxc}} \sim |\Delta\hat{T}|^{-\alpha}, \quad (6)$$

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]

$$\frac{\rho C_V}{T} = \left(\frac{d^2P}{dT^2}\right)_{\text{cxc}} - \rho \left(\frac{d^2\mu}{dT^2}\right)_{\text{cxc}}, \quad (7)$$

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. Nicoll’s analysis also predicts non-analytic behavior of the chemical potential, specifically,

$$\left(\frac{d^2\mu}{dT^2}\right)_{\text{cxc}} \sim |\Delta\hat{T}|^{-\alpha-\beta+\theta_5}, \quad (8)$$

however, the relatively large value of θ_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 2β 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 Section II, we develop a complete scaling equation of state in Section III. In Section 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 Section V, with the finding that they are equivalent up to a term involving the higher-order asymmetric correction to scaling exponent θ_5 . Additionally, we investigate the possibility of extracting the complete scaling mixing parameters from a mean-field equation of state. In Section 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

$$h_3(h_1, h_2) \approx |h_2|^{2-\alpha} g^\pm \left(\frac{h_1}{|h_2|^{2-\alpha-\beta}} \right), \quad (9)$$

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 $h_1 = h_2 = h_3 = 0$. The independent scaling fields are thermodynamically conjugate to two scaling densities, ϕ_1 and ϕ_2 , known as the “order-parameter” and the “weakly-fluctuating density” respectively. The scaling fields and densities are connected by the thermodynamic relation

$$dh_3 = \phi_1 dh_1 + \phi_2 dh_2, \quad (10)$$

so that

$$\phi_1 = \left(\frac{\partial h_3}{\partial h_1} \right)_{h_2}, \quad \phi_2 = \left(\frac{\partial h_3}{\partial h_2} \right)_{h_1}. \quad (11)$$

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

$$\phi_1 \approx \pm B_0 |h_2|^\beta, \quad (12)$$

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,

$$\phi_2 \approx -\frac{A_0^-}{1-\alpha} |h_2|^{1-\alpha} + B_{\text{cr}} |h_2|. \quad (13)$$

In these expressions A_0^- and B_0 are non-universal critical amplitudes. The term proportional to B_{cr} is an analytic fluctuation-induced contribution to ϕ_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 μ , and the pressure P , and the conjugate densities are the number density ρ and the entropy density s . The physical variables are interrelated by the Gibbs-Duhem relation

$$dP = \rho d\mu + s dT. \quad (14)$$

Consequently, the densities are derived from the pressure as

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

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

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

it is convenient to define

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

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

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

$$h_2 \simeq b_1 \Delta\hat{T} + b_2 \Delta\hat{\mu} + b_3 \Delta\hat{P}, \quad (19)$$

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

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 justification of the truncated transformations presented above is required. In this work we only consider contributions to the excess density $\Delta\hat{\rho}_d$ which are of order $|\Delta\hat{T}|$ or lower. Two second-order terms satisfy this criterion, $\Delta\hat{\mu} \Delta\hat{T}$ 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.* non-critical, 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 $\Delta\hat{\mu} \Delta\hat{P}$, $\Delta\hat{P} \Delta\hat{T}$, $\Delta\hat{P}^2$, and $\Delta\hat{\mu}^2$ 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 $\hat{s}_c = s_c / \rho_c k_B$, which is arbitrary in classical thermodynamics, and neglecting higher order terms. Specifically, we choose $\hat{s}_c = (dP/dT)_{h_1=0,c}$. These simplification can be implemented by adopting the following choice of coefficients

$$a_1 = (1 - a), \quad a_2 = -a\hat{s}_c, \quad a_3 = a, \quad (21)$$

$$b_1 = 1, \quad b_2 = b, \quad b_3 = 0, \quad (22)$$

$$c_1 = 1, \quad c_2 = -1, \quad c_3 = -\hat{s}_c, \quad c_{23} = c. \quad (23)$$

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

$$\Delta\tilde{P} = \Delta\hat{P} - \Delta\hat{\mu} - \hat{s}_c \Delta\hat{T}, \quad (24)$$

that the transformations reduce to

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

$$h_2 = \Delta\hat{T} + b \Delta\hat{\mu}, \quad (26)$$

$$h_3 = \Delta\tilde{P} + c \Delta\hat{\mu} \Delta\hat{T}. \quad (27)$$

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 Eq. (10), Eq. (14), and Eqs. (25)-(27), with the result

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

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

where ϕ_1 and ϕ_2 are given by Eqs. (12) and (13) respectively. To leading order in the asymmetry and reduced temperature these expressions are given by

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

$$\Delta\hat{s} \simeq \phi_2. \quad (31)$$

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

$$D_{2\beta} = a(B_0)^2, \quad (32)$$

$$D_{1-\alpha} = -b\frac{A_0^-}{1-\alpha}, \quad (33)$$

$$D_1 = B_{\text{cr}} + c. \quad (34)$$

We note that the leading 2β 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

$$\left(\frac{d^2\hat{\mu}}{d\hat{T}^2}\right)_{\text{cxc}} \simeq -a\left(\frac{d^2\hat{P}}{d\hat{T}^2}\right)_{\text{cxc}} = -aA_0^-|\Delta\hat{T}|^{-\alpha}, \quad (35)$$

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 Eqs. (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

$$\Delta\tilde{P}(\Delta\hat{\mu}, \Delta\hat{T}) = h_3(h_1, h_2) - c\Delta\hat{\mu}\Delta\hat{T}, \quad (36)$$

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 $\Delta\hat{\mu}$ and $\Delta\hat{T}$ can be made manifest by expanding in the asymmetric terms. If we define

$$h_3^{(0)}(\Delta\hat{\mu}, \Delta\hat{T}) = h_3(h_1 = \Delta\hat{\mu}, h_2 = \Delta\hat{T}), \quad (37)$$

$$\phi_1^{(0)}(\Delta\hat{\mu}, \Delta\hat{T}) = \left(\frac{\partial h_3}{\partial h_1}\right)_{h_1=\Delta\hat{\mu}, h_2=\Delta\hat{T}}, \quad (38)$$

$$\phi_2^{(0)}(\Delta\hat{\mu}, \Delta\hat{T}) = \left(\frac{\partial h_3}{\partial h_2}\right)_{h_1=\Delta\hat{\mu}, h_2=\Delta\hat{T}}, \quad (39)$$

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

$$h_3(h_1, h_2) \simeq h_3^{(0)} + \phi_1^{(0)}(a\Delta\tilde{P}) + \phi_2^{(0)}(b\Delta\hat{\mu}). \quad (40)$$

We note that the functions $h_3^{(0)}$, $\phi_1^{(0)}$, and $\phi_2^{(0)}$ are the same functions as h_3 , ϕ_1 , and ϕ_2 , as introduced in Eqs. (10) and (11). The superscript (0) has been added to emphasize that these functions are now being evaluated at $(\Delta\hat{\mu}, \Delta\hat{T})$ instead of at the defined variables (h_1, h_2) . Equation (27) can now be written

$$\Delta\tilde{P}(\Delta\hat{\mu}, \Delta\hat{T}) = \hat{P}_{\text{sym}} + a\hat{P}_a + b\hat{P}_b + c\hat{P}_c \quad (41)$$

where

$$\hat{P}_{\text{sym}}(\Delta\hat{\mu}, \Delta\hat{T}) = h_3^{(0)}(\Delta\hat{\mu}, \Delta\hat{T}) \quad (42)$$

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

$$\hat{P}_a(\Delta\hat{\mu}, \Delta\hat{T}) = \phi_1^{(0)}(\Delta\hat{\mu}, \Delta\hat{T})h_3^{(0)}(\Delta\hat{\mu}, \Delta\hat{T}), \quad (43)$$

$$\hat{P}_b(\Delta\hat{\mu}, \Delta\hat{T}) = \phi_2^{(0)}(\Delta\hat{\mu}, \Delta\hat{T})\Delta\hat{\mu}, \quad (44)$$

$$\hat{P}_c(\Delta\hat{\mu}, \Delta\hat{T}) = -\Delta\hat{\mu}\Delta\hat{T}. \quad (45)$$

To leading order in the asymmetry, the content of the complete scaling transformations is fully contained in the EOS given by Eq. (41). However, it is challenging to write an explicit expression for h_3 as a function of h_1 and h_2 that satisfies the analyticity requirements discussed by Griffiths [46]. The same is not true of the Helmholtz energy density $f(\rho, T)$, which can be written as an explicit function of ρ and T , at least in the context of the ϵ -expansion.

The derivation of the complete scaling EOS for the Helmholtz energy density, $\Delta\hat{f}(\Delta\hat{\rho}, \Delta\hat{T}) = (f - f_c)/\rho_c k_B T_c$, which, for brevity, we henceforth call the Helmholtz energy, closely follows the previous derivation for $\Delta\hat{P}(\Delta\hat{\mu}, \Delta\hat{T})$. The Helmholtz energy and pressure are related by the Legendre transformation

$$f(\rho, T) = \mu\rho - P. \quad (46)$$

The analogous quantity in the symmetric Ising system, ψ , is defined by

$$\psi(\phi_1, h_2) = h_1\phi_1 - h_3. \quad (47)$$

Using Eq. (11) one can show that

$$h_1 = \left(\frac{\partial \psi}{\partial \phi_1} \right)_{h_2}, \quad \phi_2 = - \left(\frac{\partial \psi}{\partial h_2} \right)_{\phi_1}. \quad (48)$$

Applying the transformations Eqs. (46) and (47) to Eq. (27), we find, with the aid of the definition

$$\Delta \tilde{f} = \Delta \hat{f} - \hat{\mu}_c \Delta \hat{\rho} + \hat{s}_c \Delta \hat{T}, \quad (49)$$

that the Helmholtz energy can be written as

$$\Delta \tilde{f} = (1 + a\phi_1)\psi + b\phi_2 h_1. \quad (50)$$

Whereas Eq. (27) establishes the relationship between the pressure P and the symmetric potential h_3 , the above equation establishes the analogous relationship between the Helmholtz energy f and the symmetric potential ψ . We note that the relationship between reduced potentials can be compactly expressed as

$$\Delta \tilde{f} = \Delta \hat{\mu} \Delta \hat{\rho} - \Delta \tilde{P}. \quad (51)$$

To obtain an expression for $\Delta \tilde{f}$ which is manifestly dependent on $\Delta \hat{\rho}$ and $\Delta \hat{T}$, the potential ψ , which is naturally a function of ϕ_1 and h_2 , can be expanded in asymmetric terms, as was done for h_3 in Eq. (40). If we define

$$\psi^{(0)}(\Delta \hat{\rho}, \Delta \hat{T}) = \psi(\phi_1 = \Delta \hat{\rho}, h_2 = \Delta \hat{T}), \quad (52)$$

$$h_1^{(0)}(\Delta \hat{\rho}, \Delta \hat{T}) = \left(\frac{\partial \psi}{\partial \phi_1} \right)_{\phi_1 = \Delta \hat{\rho}, h_2 = \Delta \hat{T}}, \quad (53)$$

$$\phi_2^{(0)}(\Delta \hat{\rho}, \Delta \hat{T}) = - \left(\frac{\partial \psi}{\partial h_2} \right)_{\phi_1 = \Delta \hat{\rho}, h_2 = \Delta \hat{T}}, \quad (54)$$

then the double Taylor expansion of ψ around $\phi_1 = \Delta \hat{\rho}$ and $h_2 = \Delta \hat{T}$ is given by

$$\psi(\phi_1, h_2) \simeq \psi^{(0)} + h_1^{(0)}(c\Delta \hat{T} - a\Delta \hat{\rho}^2 - 2b\phi_2^{(0)}). \quad (55)$$

Again, we note that the functions $\psi^{(0)}$, $h_1^{(0)}$, and $\phi_2^{(0)}$ are the same functions as ψ , h_1 , and ϕ_2 , as introduced in Eqs. (47) and (48). The superscript (0) has been added to emphasize that these functions are now being evaluated at $(\Delta \hat{\rho}, \Delta \hat{T})$ instead of at the defined variables (ϕ_1, h_2) . Eventually, we will compare the Helmholtz energy derived from the complete scaling transformations, Eqs. (25) - (27), with that resulting from a field-theoretic approach. In order to distinguish the two, we will add a subscript CS to the complete scaling Helmholtz energy. Equation (50) can now be rewritten as

$$\Delta \tilde{f}_{\text{CS}}(\Delta \hat{\rho}, \Delta \hat{T}) = \hat{f}_{\text{sym}} + a\hat{f}_a^{\text{CS}} + b\hat{f}_b^{\text{CS}} + c\hat{f}_c^{\text{CS}}, \quad (56)$$

where we have introduced the definition

$$\hat{f}_{\text{sym}}(\Delta \hat{\rho}, \Delta \hat{T}) = \psi^{(0)}(\Delta \hat{\rho}, \Delta \hat{T}), \quad (57)$$

which is the leading symmetric (lattice gas) Helmholtz energy, and where the asymmetric corrections are given by

$$\hat{f}_a^{\text{CS}}(\Delta \hat{\rho}, \Delta \hat{T}) = \Delta \hat{\rho} \psi^{(0)}(\Delta \hat{\rho}, \Delta \hat{T}) - \Delta \hat{\rho}^2 h_1^{(0)}(\Delta \hat{\rho}, \Delta \hat{T}), \quad (58)$$

$$\hat{f}_b^{\text{CS}}(\Delta \hat{\rho}, \Delta \hat{T}) = -\phi_2^{(0)}(\Delta \hat{\rho}, \Delta \hat{T}) h_1^{(0)}(\Delta \hat{\rho}, \Delta \hat{T}), \quad (59)$$

$$\hat{f}_c^{\text{CS}}(\Delta \hat{\rho}, \Delta \hat{T}) = \Delta \hat{T} h_1^{(0)}(\Delta \hat{\rho}, \Delta \hat{T}). \quad (60)$$

We will refer to Eq. (56) as the complete scaling EOS. Expressions for \hat{f}_a^{CS} , \hat{f}_b^{CS} , and \hat{f}_c^{CS} , based on an ϵ -expansion analysis of the symmetric LGW Hamiltonian, are given in the mean-field approximation in the following subsection and are presented to order ϵ^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 ϵ^2 [48], may be used instead of the explicit ϵ -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 ψ , 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 when only the leading asymptotic terms are considered. Hence, we will now restrict \hat{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 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

$$\hat{f}_{\text{sym, mf}} = \psi_{\text{mf}}^{(0)} = -\frac{(\Delta \hat{T})^2}{2u} + \frac{1}{2}\Delta \hat{T} \Delta \hat{\rho}^2 + \frac{u}{4!}\Delta \hat{\rho}^4. \quad (61)$$

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

$$h_{1, \text{mf}}^{(0)} = \Delta \hat{T} \Delta \hat{\rho} + \frac{u}{6}\Delta \hat{\rho}^3, \quad (62)$$

and

$$\phi_{2, \text{mf}}^{(0)} = \frac{\Delta \hat{T}}{u} - \frac{1}{2}\Delta \hat{\rho}^2. \quad (63)$$

This last equation is the mean-field approximation of Eq. (13) with $B_{\text{cr}} = 0$. The asymmetric contributions to the

Helmholtz energy are found from the definitions given in Eqs. (58)-(60) to be

$$\hat{f}_{a,\text{mf}}^{\text{CS}} = -\frac{1}{2}\frac{(\Delta\hat{T})^2}{u}\Delta\hat{\rho} - \frac{1}{2}\Delta\hat{T}\Delta\hat{\rho}^3 - \frac{u}{8}\Delta\hat{\rho}^5, \quad (64)$$

$$\hat{f}_{b,\text{mf}}^{\text{CS}} = -\frac{(\Delta\hat{T})^2}{u}\Delta\hat{\rho} + \frac{1}{3}\Delta\hat{T}\Delta\hat{\rho}^3 + \frac{u}{12}\Delta\hat{\rho}^5, \quad (65)$$

$$\hat{f}_{c,\text{mf}}^{\text{CS}} = (\Delta\hat{T})^2\Delta\hat{\rho} + \frac{u}{6}\Delta\hat{T}\Delta\hat{\rho}^3. \quad (66)$$

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

$$\begin{aligned} \Delta\tilde{f}_{\text{CS,mf}} &= \hat{f}_{\text{sym,mf}} + (cu - b - \frac{1}{2}a)\frac{(\Delta\hat{T})^2}{u}\Delta\hat{\rho} \\ &+ \frac{1}{3!}(2b - 3a + cu)\Delta\hat{T}\Delta\hat{\rho}^3 + \frac{u}{5!}(10b - 15a)\Delta\hat{\rho}^5. \end{aligned} \quad (67)$$

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 (FT) approach, Nicoll has analyzed the addition of asymmetric terms to the symmetric LGW Hamiltonian, such that the full Hamiltonian is of the form [16]

$$\mathcal{H} = \mathcal{H}_{\text{sym}} + \mathcal{H}_{\text{asym}}, \quad (68)$$

where the symmetric Hamiltonian is given in terms of the spatially dependent field variable $\varphi(\mathbf{x})$ by

$$\mathcal{H}_{\text{sym}} = -\frac{(\Delta\hat{T})^2}{2u} + \frac{1}{2}(\Delta\hat{T})\varphi^2 + \frac{u}{4!}\varphi^4 - \frac{1}{2}\varphi\nabla^2\varphi, \quad (69)$$

and where the asymmetric portion can be written

$$\mathcal{H}_{\text{asym}} = u_1O_1 + u_3O_3 + u_5O_5 + u_\lambda O_\lambda, \quad (70)$$

with

$$O_1 = \frac{(\Delta\hat{T})^2}{u}\varphi, \quad O_3 = \frac{1}{3!}(\Delta\hat{T})\varphi^3 \quad (71)$$

$$O_5 = \frac{u}{5!}\varphi^5, \quad O_\lambda = -\frac{1}{3!}\varphi^2\nabla^2\varphi. \quad (72)$$

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

$$\Delta\tilde{P} = \ln \left\{ \int \mathcal{D}\varphi \exp \left[\int d\mathbf{x} (\varphi h_1 - \mathcal{H}) \right] \right\}. \quad (73)$$

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 $h_1 = \Delta\hat{\mu} - \Delta\hat{\mu}_{\text{cxc}}(T)$ and $h_1 = \Delta\hat{P} - \Delta\hat{P}_{\text{cxc}}(T)$ or a combination of the two appear to be satisfactory, where the subscript cxc denotes the conditions of phase coexistence. However, the ordering field cannot 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.* $d^2\mu_{\text{cxc}}/dT^2 \sim |\Delta\hat{T}|^{-\alpha}$. If $\mu_{\text{cxc}}(T)$ is analytic, *i.e.* no Yang-Yang anomaly, the ordering field can be taken as

$$h_1 = \Delta\hat{\mu} - \Delta\hat{\mu}_{\text{cxc}}(T). \quad (74)$$

A term proportional to $\Delta\hat{P} - \Delta\hat{P}_{\text{cxc}}(T)$, *i.e.* pressure mixing, cannot be included, since $\Delta\hat{P}_{\text{cxc}}(T)$ is not analytic in T . In this case, as discussed below Eq. (20), the term $\Delta\hat{\mu}_{\text{cxc}}(T)$ can be absorbed into the regular part of the thermodynamic potential leaving

$$h_1 = \Delta\hat{\mu}, \quad (75)$$

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 $\langle\varphi\rangle = \Delta\hat{\rho}$ in the absence of a Yang-Yang anomaly.

In contrast, when $\hat{\mu}_{\text{cxc}}(T)$ is non-analytic in T at the critical point, Eq. (74) is no longer valid. Instead, the pressure is ‘‘mixed’’ into h_1 as

$$h_1 = [\Delta\hat{\mu} - \Delta\hat{\mu}_{\text{cxc}}(T)] + a[\Delta\hat{P} - \Delta\hat{P}_{\text{cxc}}(T)], \quad (76)$$

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 \hat{s}_c , $\Delta\hat{\mu}_{\text{cxc}}(T) \approx -a\Delta\tilde{P}_{\text{cxc}}(T)$. The pressure mixing ensures the analyticity of h_1 when $\hat{\mu}_{\text{cxc}}(T)$ is non-analytic. By taking a functional derivative of Eq. (73) with respect to h_1 , we find that

$$\langle\varphi\rangle \simeq \Delta\hat{\rho} - a(\Delta\hat{\rho})^2. \quad (77)$$

The relationship between the Helmholtz energy, $\Delta\tilde{f} = \Delta\tilde{f}(\langle\varphi\rangle, \Delta\hat{T})$, and the Hamiltonian is found by applying a Legendre transformation, Eq. (51), to Eq. (73), with the result

$$\Delta\tilde{f} = -\ln \left\{ \int \mathcal{D}\varphi \exp \left[\int d\mathbf{x} (\varphi h_1 - \Delta\hat{\mu}\Delta\hat{\rho} - \mathcal{H}) \right] \right\}. \quad (78)$$

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, \hat{f}_i^{FT} , to the total Helmholtz energy, which may now be written as

$$\Delta\tilde{f} = \hat{f}_{\text{sym}}(\langle\varphi\rangle, \Delta\hat{T}) + \Delta\hat{\mu}\Delta\hat{\rho} - h_1\langle\varphi\rangle + u_1\hat{f}_1^{\text{FT}} + u_3\hat{f}_3^{\text{FT}} + u_5\hat{f}_5^{\text{FT}} + u_\lambda\hat{f}_\lambda^{\text{FT}}, \quad (79)$$

where the asymmetry coefficients, u_i , were introduced in the definition of the asymmetric LGW Hamiltonian, Eq. (70). We note that \hat{f}_{sym} in this expression only includes the leading asymptotic 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

$$\Delta\tilde{f}_{\text{FT}}(\Delta\hat{\rho}, \Delta\hat{T}) = \hat{f}_{\text{sym}} + a\hat{f}_a^{\text{CS}} + u_1\hat{f}_1^{\text{FT}} + u_3\hat{f}_3^{\text{FT}} + u_5\hat{f}_5^{\text{FT}} + u_\lambda\hat{f}_\lambda^{\text{FT}}, \quad (80)$$

where \hat{f}_a^{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 \hat{f}_3^{FT} , \hat{f}_5^{FT} , and $\hat{f}_\lambda^{\text{FT}}$ are given in the mean-field approximation in the following subsection and are presented to order ϵ^2 in the Appendix.

A. FT EOS in the mean-field approximation

In the mean-field approximation, the \hat{f}_i^{FT} are given by

$$\hat{f}_{1,\text{mf}}^{\text{FT}} = \frac{(\Delta\hat{T})^2}{u}\Delta\hat{\rho}, \quad \hat{f}_{3,\text{mf}}^{\text{FT}} = \frac{1}{3!}\Delta\hat{T}\Delta\hat{\rho}^3 \quad (81)$$

$$\hat{f}_{5,\text{mf}}^{\text{FT}} = \frac{u}{5!}\Delta\hat{\rho}^5, \quad \hat{f}_{\lambda,\text{mf}}^{\text{FT}} = 0. \quad (82)$$

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

$$\Delta\tilde{f}_{\text{FT,mf}} = \hat{f}_{\text{sym,mf}} + (u_1 - \frac{1}{2}a)\frac{(\Delta\hat{T})^2}{u}\Delta\hat{\rho} + \frac{1}{3!}(u_3 - 3a)\Delta\hat{T}\Delta\hat{\rho}^3 + \frac{u}{5!}(u_5 - 15a)\Delta\hat{\rho}^5, \quad (83)$$

where $\hat{f}_{\text{sym,mf}}$ 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 (ρ_c, T_c) the result is expressed with only a single coefficient for each term, for example

$$\Delta\tilde{f}_{\text{mf}} = \hat{f}_{\text{sym,mf}} + k_1\frac{(\Delta\hat{T})^2}{u}\Delta\hat{\rho} + \frac{1}{3!}k_3\Delta\hat{T}\Delta\hat{\rho}^3 + \frac{u}{5!}k_5\Delta\hat{\rho}^5. \quad (84)$$

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, Eq. (70), since they differ by terms proportional to the mixing coefficient a . Of course, the two are related by

$$k_1 = u_1 - \frac{1}{2}a, \quad (85)$$

$$k_3 = u_3 - 3a, \quad (86)$$

$$k_5 = u_5 - 15a. \quad (87)$$

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 Eq. (56) and Eq. (80) respectively. First, we note that, in the context of the ϵ -expansion, \hat{f}_1^{FT} is proportional to $\hat{f}_{1,\text{mf}}^{\text{FT}}$. Therefore \hat{f}_1^{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)), \hat{f}_b^{CS} and \hat{f}_c^{CS} , which are expressed in terms of the symmetric functions h_1 and ϕ_2 in Eqs. (59) and (60), can also be expressed in terms of \hat{f}_1^{FT} , \hat{f}_3^{FT} , \hat{f}_5^{FT} , and $\hat{f}_\lambda^{\text{FT}}$ as derived from the asymmetric LGW Hamiltonian, and introduced in Eq. (79). Specifically one has

$$\hat{f}_c^{\text{CS}} = u\left(\hat{f}_1^{\text{FT}} + \hat{f}_3^{\text{FT}}\right), \quad (88)$$

$$\hat{f}_b^{\text{CS}} = -\hat{f}_1^{\text{FT}} + 2\hat{f}_3^{\text{FT}} + 10\hat{f}_5^{\text{FT}} + 3\hat{f}_\lambda^{\text{FT}}. \quad (89)$$

These equalities can be verified in the mean-field approximation by combining Eqs. (64) - (66) and Eqs. (81) and (82), and to order ϵ^2 using the results given in the Appendix. The simplicity of the expression for \hat{f}_c^{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 $\varphi \rightarrow \varphi - (u_3/u)\Delta\hat{T}$. This simply leads to a shift proportional to $\Delta\hat{T}$ in the order parameter $\langle\varphi\rangle$. Interestingly, Eqs. (88) and (89) are quite general and can be proven outside the context of the ϵ expansion [16]. Like \hat{f}_b^{CS} and \hat{f}_c^{CS} , the pressure-mixing term \hat{f}_a^{CS} can be expressed as a linear combination of \hat{f}_1^{FT} , \hat{f}_3^{FT} , \hat{f}_5^{FT} , and $\hat{f}_\lambda^{\text{FT}}$ through order ϵ [45]. However, this type of relationship breaks down for \hat{f}_a^{CS} at order ϵ^2 .

Equations (88) and (89) for \hat{f}_b^{CS} and \hat{f}_c^{CS} and our ability to select u_1 allow us to rewrite the FT EOS, Eq. (80),

as

$$\Delta \tilde{f}_{\text{FT}} = \hat{f}_{\text{sym}} + a \hat{f}_a^{\text{CS}} + b \hat{f}_b^{\text{CS}} + c \hat{f}_c + u_5^{\text{eff}} \hat{f}_5, \quad (90)$$

where

$$cu = u_3 - (2/3)u_\lambda. \quad (91)$$

$$b = (1/3)u_\lambda, \quad (92)$$

$$u_5^{\text{eff}} = u_5 - \frac{10}{3}u_\lambda, \quad (93)$$

The term proportional to u_5^{eff} is responsible for the asymmetric correction-to-scaling exponent θ_5 introduced in Eq. (4). In particular, in Eq. (4), $D_{\beta+\theta_5}$ is proportional to u_5^{eff} [16]. The relationship between the FT EOS, Eq. (80), and the complete scaling EOS, Eq. (56), can be compactly written as

$$\Delta \tilde{f}_{\text{FT}} = \Delta \tilde{f}_{\text{CS}} + u_5^{\text{eff}} \hat{f}_5^{\text{FT}}. \quad (94)$$

and the corresponding excess density can be written

$$\Delta \hat{\rho}_d \approx D_{1-\alpha} |\Delta \hat{T}|^{1-\alpha} + D_{2\beta} |\Delta \hat{T}|^{2\beta} + D_1 |\Delta \hat{T}| + D_{\beta+\theta_5} |\Delta \hat{T}|^{\beta+\theta_5}, \quad (95)$$

where the coefficients and exponents are the same as those introduced in Section I. We note that the above expression matches that proposed by Fisher and coworkers [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_5^{eff} prohibits an exact mapping. This reflects the fact that θ_5 is an independent critical exponent and cannot be expressed in terms of Ising exponents. However, since the θ_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_5^{eff} cannot 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

$$\Delta \tilde{f}_{\text{FT,mf}} = \Delta \tilde{f}_{\text{CS,mf}} + u_5^{\text{eff}} \frac{u}{5!} \Delta \hat{\rho}^5, \quad (96)$$

where $\Delta \tilde{f}_{\text{FT,mf}}$ and $\Delta \tilde{f}_{\text{CS,mf}}$ are given by Eq. (83) and Eq. (67) respectively. As previously noted, the term proportional to u_5^{eff} breaks the full isomorphism between the symmetric and asymmetric Helmholtz energies. In the

mean-field approximation, the θ_5 contribution stemming from this term is of the same order as the other leading asymmetric terms, *e. g.* $|\Delta \hat{T}|^{\beta+\theta_5}$ is proportional to $|\Delta \hat{T}|$ in the excess density, and therefore it cannot 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 $k_1 = k_3 = 0$ [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

$$\Delta \tilde{f}_{\text{vdW,mf}} = \hat{f}_{\text{sym,mf}} + u_5^{\text{eff}} \frac{u}{5!} \Delta \hat{\rho}^5, \quad (97)$$

where $\hat{f}_{\text{sym,mf}}$ is given by Eq. (61). As a consequence, all asymmetry in the van der Waals excess density comes entirely from the $|\Delta \hat{T}|^{\beta+\theta_5}$ term. If u_5^{eff} were simply neglected for the van der Waals EOS, which would imply that complete scaling as formulated in Section II is exact, one instead finds non-zero 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_λ could be proportional to u_5 , 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 $u_5^{\text{eff}} = u_5 - (10/3)u_\lambda = 0$. For this case there is a special relationship between the complete scaling mixing parameters and the mean-field expansion coefficients introduced in Eq. (84):

$$k_1 = cu - b - \frac{1}{2}a, \quad (98)$$

$$k_3 = 2b - 3a + cu, \quad (99)$$

$$k_5 = 10b - 15a, \quad (100)$$

which can be found by combining Eq. (67) and Eq. (84). These relationships can be inverted to yield expressions for the mixing coefficients in terms of the Hamiltonian coefficients. As an example, if we returning to the case of the van der Waals EOS, we find

$$a = \frac{3}{20}k_5, \quad (101)$$

$$b = \frac{1}{8}k_5, \quad (102)$$

$$cu = \frac{1}{5}k_5. \quad (103)$$

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 $k_1 = -1/2a$, then $cu = b$ and we are left with the mean-field relations of Wang

and Anisimov [24]

$$a = \frac{2}{3}k_3 - \frac{1}{5}k_5, \quad (104)$$

$$b = k_3 - \frac{1}{5}k_5, \quad (105)$$

who omitted the non-linear mixing contribution $\Delta\hat{\mu}\Delta\hat{T}$ 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 Section 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 non-analytic. 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 θ_5 . The relationship between the two equations of state is compactly summarized by Eq. (94). For many practical applications, the contribution from θ_5 can be neglected. In this regime, the complete scaling and FT approaches are equivalent. However, as emphasized in Section V, care is required in applying this simplification to the mean-field approximation, because the terms involving θ_5 are the same order as the other leading asymmetric corrections.

There is an analogy between the asymmetric correction-to-scaling exponent θ_5 and the Wegner correction-to-scaling exponent $\Delta \simeq \epsilon/2$ [51]. 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 [52]

$$h_{3,\text{sym}} \approx |h_2|^{2-\alpha} g^\pm(z) [1 + |h_2|^\Delta g_1^\pm(z)], \quad (106)$$

where $z = h_1/|h_2|^{2-\alpha-\beta}$ and $g_1^\pm \propto (u^* - u)$. 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,

$$h_3 \approx |h_2|^{2-\alpha} g^\pm(z) [1 + |h_2|^{\theta_5} g_{\text{asym}}^\pm(z)], \quad (107)$$

where $g_{\text{asym}} \propto u_5^{\text{eff}} = u_5 - (10/3)u_\lambda$. As in the case of the Wegner correction, which is associated with an additional critical amplitude $u^* - u$, the θ_5 exponent is associated with the new critical amplitude u_5^{eff} . We note that if $u_5 = (10/3)u_\lambda$, 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

$$h_3 \approx |h_2|^{2-\alpha} g^\pm(z) [1 + |h_2|^\Delta g_1^\pm(z) + |h_2|^{\theta_5} g_{\text{asym}}^\pm(z)]. \quad (108)$$

However, there is a significant difference between these two corrections-to-scaling. Unlike θ_5 , the exponent Δ 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 of θ_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

$$\hat{\rho} = 1 + a\phi_1, \quad (109)$$

$$x = \frac{x_c + (1-a)\phi_1 + b\phi_2}{1 + a\phi_1}, \quad (110)$$

$$\hat{\rho}x = x_c + (1-a)\phi_1 + b\phi_2, \quad (111)$$

where, along the coexistence curve, ϕ_1 and ϕ_2 are given Eqs. (12) and (13). Complete scaling predicts a 2β 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 φ in Section IV to should be connected to the mole fraction x by

$$\langle \varphi \rangle = \hat{x} - a\hat{x}^2. \quad (112)$$

As discussed by Bertrand and Anisimov [25], the asymmetric-gradient coefficient u_λ also contributes to the asymmetry of the correlation length ξ via,

$$\xi^2 \simeq (\xi_{\text{sym}})^2 [1 \pm (3a + u_\lambda) B_0 |\Delta\hat{T}|^\beta], \quad (113)$$

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_λ independently. These values could be compared those those obtained from excess density data, to conclusively determine the extent to which neglecting u_5^{eff} is 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 singularity characterized by the exponent $-\alpha$. Similarly, $d^2\mu_{\text{cxc}}/dT^2$ 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, Eq. (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 Section 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 Section V shed light on a recent suggestion [50], based on a mean-field-like analysis of an asymmetric LGW Hamiltonian, that complete scaling arises naturally from the FT analysis of the asymmetric LGW Hamiltonian. Just like the work of Wang and Anisimov [24], the results presented in [50] are only applicable to the specific case $u_5^{\text{eff}} = 0$, but not to the general case. As mentioned in the introduction, evidence for a Yang-Yang anomaly has been found in computer simulations of model interaction potentials. However, a full theoretical treatment of these interaction potentials with an eye towards asymmetry have yet to be undertaken and consequently the exact ‘‘microscopic’’ origin of the Yang-Yang anomaly remains a topic for future work. Hopefully, such work would shed light on the strong correlation between the mixing coefficient a and the ratio 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 A: Order ϵ^2 results

In this Appendix we give expressions to order ϵ^2 , in the ϵ -expansion, where $\epsilon = 4 - d$ and d is the spatial dimensionality, for \hat{f}_a^{CS} , \hat{f}_b^{CS} , and \hat{f}_c^{CS} as defined by Eqs. (58) - (60), and for \hat{f}_3^{FT} , \hat{f}_5^{FT} , and $\hat{f}_\lambda^{\text{FT}}$, which were introduced in Eq. (79). The ϵ -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 Sections III A, IV A, V A [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 ϵ^2 . In this Appendix we provide the material necessary to verify this statement.

To order ϵ^2 , the symmetric Helmholtz energy based on the ϵ -expansion of the symmetric LGW Hamiltonian, Eq. (69), is given by

$$\psi(\Delta\hat{\rho}, \Delta\hat{T}) = \psi_{\text{mf}}^{(0)} - \frac{1}{2} \frac{\kappa^4}{\epsilon} \left[\frac{\kappa^{-\epsilon}}{1 - \frac{\epsilon}{4}} - B_0 \right] \frac{\kappa^4}{8} + \frac{u}{8} \kappa^4 (L+1)^2 + \frac{u^2}{8} \kappa^2 \Delta\hat{\rho}^2 (L^2 - f), \quad (\text{A1})$$

where, by definition,

$$\kappa^2 = \Delta\hat{T} + \frac{u}{2} \Delta\hat{\rho}^2, \quad (\text{A2})$$

$L = \ln(\kappa^2)$, $f = 4 + \pi^2 + 8\lambda$ ($\lambda \simeq 1.17$), $B_0 = 1 + \epsilon/2$, 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 ϕ_2 furnished by Eq. (48), one finds that

$$h_1(\Delta\hat{\rho}, \Delta\hat{T}) = h_{1,\text{mf}}^{(0)} + u \Delta\hat{\rho} \frac{\kappa^2}{\epsilon} [\kappa^{-\epsilon} - B_0] + \frac{u^2}{4} \kappa^2 \Delta\hat{\rho} [(L+1)(L+2) + L^2 - f] + \frac{u^3}{8} \Delta\hat{\rho}^3 (L^2 - f + 2L), \quad (\text{A3})$$

and

$$\phi_2(\Delta\hat{\rho}, \Delta\hat{T}) = \phi_{2,\text{mf}}^{(0)} + \frac{\kappa^2}{\epsilon} [\kappa^{-\epsilon} - B_0] - \frac{u}{4} \kappa^2 (L+1)(L+2) - \frac{u^2}{8} \Delta\hat{\rho}^2 (L^2 - f + 2L), \quad (\text{A4})$$

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

$$\delta h_1(\Delta\hat{\rho}, \Delta\hat{T}) = h_1(\Delta\hat{\rho}, \Delta\hat{T}) - h_{1,\text{mf}}^{(0)}(\Delta\hat{\rho}, \Delta\hat{T}), \quad (\text{A5})$$

and

$$\delta\psi(\Delta\hat{\rho}, \Delta\hat{T}) = \psi(\Delta\hat{\rho}, \Delta\hat{T}) - \psi_{\text{mf}}^{(0)}(\Delta\hat{\rho}, \Delta\hat{T}). \quad (\text{A6})$$

The pieces of the complete scaling Helmholtz energy, \hat{f}_a^{CS} , \hat{f}_b^{CS} , and \hat{f}_c^{CS} , can be calculated to order ϵ^2 through Eqs. (58)-(60), with the following results,

$$\hat{f}_a^{\text{CS}}(\Delta\hat{\rho}, \Delta\hat{T}) = \hat{f}_{a,\text{mf}}^{\text{CS}} + (\Delta\hat{\rho}) \delta\psi(\Delta\hat{\rho}, \Delta\hat{T}) - (\Delta\hat{\rho})^2 \delta h_1(\Delta\hat{\rho}, \Delta\hat{T}), \quad (\text{A7})$$

$$\begin{aligned} \hat{f}_b^{\text{CS}}(\Delta\hat{\rho}, \Delta\hat{T}) &= \hat{f}_{b,\text{mf}}^{\text{CS}} + \frac{2}{3}\Delta\hat{\rho}^2\delta h_1(\Delta\hat{\rho}, \Delta\hat{T}) \\ &+ \frac{u}{4}\Delta\hat{\rho}\kappa^4 \left[(L+1)^2 + \left(\frac{u}{3}\Delta\hat{\rho}^2 - \kappa^2 \right) (L^2 - f) \right], \end{aligned} \quad (\text{A8})$$

and

$$\hat{f}_c^{\text{CS}}(\Delta\hat{\rho}, \Delta\hat{T}) = \hat{f}_{c,\text{mf}}^{\text{CS}} + (\Delta\hat{T})\delta h_1(\Delta\hat{\rho}, \Delta\hat{T}), \quad (\text{A9})$$

where $\hat{f}_{a,\text{mf}}^{\text{CS}}$, $\hat{f}_{b,\text{mf}}^{\text{CS}}$, and $\hat{f}_{c,\text{mf}}^{\text{CS}}$ are given by Eqs. (64) - (66).

The expressions, resulting from an ϵ -expansion analysis of the asymmetric LGW Hamiltonian, Eq. (70), for the asymmetric contributions to the Helmholtz energy in Eq. (79), are

$$\begin{aligned} \hat{f}_5^{\text{FT}}(\Delta\hat{\rho}, \Delta\hat{T}) &= \hat{f}_{5,\text{mf}}^{\text{FT}} + \frac{1}{6}\Delta\hat{\rho}^2\delta h_1(\Delta\hat{\rho}, \Delta\hat{T}) \\ &+ \frac{u}{8}\kappa^2\Delta\hat{\rho} \left[\kappa^2 (L+1)^2 + \frac{2}{3}u\Delta\hat{\rho}^2 (L^2 - f) \right], \end{aligned} \quad (\text{A10})$$

$$\hat{f}_3^{\text{FT}}(\Delta\hat{\rho}, \Delta\hat{T}) = \hat{f}_{3,\text{mf}}^{\text{FT}} + \frac{\Delta\hat{T}}{u}\delta h_1(\Delta\hat{\rho}, \Delta\hat{T}), \quad (\text{A11})$$

and

$$\begin{aligned} \hat{f}_\lambda^{\text{FT}}(\Delta\hat{\rho}, \Delta\hat{T}) &= \hat{f}_{\lambda,\text{mf}}^{\text{FT}} - \frac{2}{3}\frac{\kappa^2}{u}\delta h_1(\Delta\hat{\rho}, \Delta\hat{T}) \\ &- \frac{u}{6}\kappa^2\Delta\hat{\rho} \left\{ \frac{3}{2}u\Delta\hat{\rho}^2 (L^2 - f) \right. \\ &\left. + \kappa^2 \left[2(L+1)^2 + \frac{1}{2}(L^2 - f) \right] \right\}, \end{aligned} \quad (\text{A12})$$

where $\hat{f}_{5,\text{mf}}^{\text{FT}}$, $\hat{f}_{3,\text{mf}}^{\text{FT}}$, and $\hat{f}_{\lambda,\text{mf}}^{\text{FT}}$ are given by Eqs. (81) and (82). The relationships between \hat{f}_b^{CS} , \hat{f}_c^{CS} , and \hat{f}_3^{FT} , \hat{f}_5^{FT} , and $\hat{f}_\lambda^{\text{FT}}$, given by Eqs. (88) and (89), can now be readily verified to order ϵ^2 with the expression presented in this Appendix.

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