Complete Scaling for Inhomogeneous Fluids

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"Complete scaling," which maps asymmetric fluid criticality onto the symmetric Ising model, is extended to spatially inhomogeneous fluids. This extension enables us to obtain a fluctuation-modified asymmetric interfacial density profile, which incorporates leading effects from the asymmetry of fluid phase coexistence and the asymmetry of the correlation length. The derived asymmetric interfacial profile is used to calculate Tolman's length, the diverging coefficient of the curvature correction to the surface tension. The amplitude of the divergent Tolman length is found to depend on the asymmetry of the correlation length.

Describing real systems by "ideal," highly simplified, theoretical models without losing essential physical information is a ubiquitous challenge in the quantitative description of matter. One example is the mapping of asymmetric fluid criticality onto the symmetric Ising or lattice-gas model which is invariant with respect to the sign of the order parameter. Fisher and co-workers showed that the thermodynamics of critical phenomena in fluids, commonly exhibiting asymmetric phase behavior, can be consistently described by mixing all physical-field variables into the three Ising-model theoretical fields [1]. This recent formulation of fluid criticality, known as complete scaling, is supported by both experiment [2–4] and simulations [5]. In particular, complete scaling predicts a new leading-order singular-contribution to the fluid mean density as a function of temperature, namely,

$$\frac{(\rho' + \rho'')}{2\rho_c} - 1 \approx D|\Delta\hat{T}|^{2\beta}, \qquad (1)$$

where ρ' and ρ'' are the liquid and vapor densities, ρ_c is the critical density, $\Delta\hat{T} = (T - T_c)/T_c$ is the reduced distance to the critical temperature T_c, $\beta \simeq 0.326$ is an Ising universal critical exponent, and D is a system-dependent coefficient, the magnitude of which is especially significant in highly asymmetric ionic and polymeric fluids [2]. Here and below, the symbol $\approx$ indicates asymptotically equal, while the symbol $\simeq$ means approximately equal.

Another important consequence of complete scaling is the divergence of Tolman's length δ, the coefficient in the first curvature correction to the surface tension σ, that is,

$$\sigma(R) = \sigma_\infty\left(1 - \frac{2\delta}{R} + \dots\right), \qquad (2)$$

where R is the radius of a spherical liquid droplet, taken equal to the radius of the surface of tension and σ_∞ is the surface tension of a planar ($R = \infty$) interface [6]. Based on complete-scaling arguments, Anisimov proposed the phenomenological expression [7]

$$\frac{\delta}{2\xi} \simeq -\frac{\rho' + \rho'' - 2\rho_c}{\rho' - \rho''}, \qquad (3)$$

where 2ξ is the "thickness" of the interface, proportional to the correlation length $\xi \propto |\Delta\hat{T}|^{-\nu}$ with an Ising universal critical exponent $\nu \simeq 0.630$. [8]. Since $\rho' - \rho'' \propto |\Delta\hat{T}|^\beta$, Eq. (3) predicts a leading singularity in Tolman's length, $\delta \propto D|\Delta\hat{T}|^{\beta-\nu}$, with $\beta - \nu \simeq -0.304$.

However, complete scaling has only been formulated for thermodynamic properties of homogeneous phases. In this Letter, we propose an extension of complete scaling to nonuniform asymmetric fluids. This generalized complete scaling enables us to derive the asymmetric fluctuation-modified interfacial density profile of two coexisting near-critical fluid phases through the well-known symmetric order-parameter profile of the Ising model, in spite of the fact that more direct approaches to this calculation are prohibitively difficult. The asymmetric profile is then applied to investigate the divergence of Tolman's length, in particular, the degree of universality of a new critical-amplitude ratio. Additionally, previous purely thermodynamic descriptions of Tolman's length are shown to be inadequate. An experiment is proposed to determine the asymmetry in the correlation length and the effect of this asymmetry on Tolman's length.

Hart extended thermodynamics to spatially inhomogeneous systems by including the density gradient $\nabla\rho$ and its conjugate field **w** as additional thermodynamic variables [9]. The field **w** represents the thermodynamic force required to establish a density gradient. Thus, for an inhomogeneous fluid, the Gibbs-Duhem relation gains an additional gradient-dependent term:

$$d\hat{P} = \hat{\rho}d\hat{\mu} + \hat{s}d\hat{T} + \hat{\nabla}\hat{\rho}\cdot d\hat{\mathbf{w}}. \qquad (4)$$

In this relation the variables for pressure $\hat{P}$, density $\hat{\rho}$, chemical potential $\hat{\mu}$, temperature $\hat{T}$, entropy density $\hat{s}$, and the gradient terms are made dimensionless via

$\hat{P} = P/\rho_c k_B T_c$, $\hat{\rho} = \rho/\rho_c$, $\hat{\mu} = \mu/k_B T_c$, $\hat{T} = T/T_c$, $\hat{s} = s/\rho_c k_B$, $\hat{\nabla}\hat{\rho} = (m^{1/2}\nabla\rho)/\rho_c$, and $\hat{\mathbf{w}} = \mathbf{w}/(m^{1/2}k_B T_c)$, where k_B is Boltzmann's constant and m is a parameter which determines the amplitude of the correlation length ξ [8]. If the dimensionless Helmholtz energy density $\hat{f} = f/\rho_c k_B T_c$ is expanded in terms of $\Delta\hat{\rho} = (\rho - \rho_c)/\rho_c$ and $\hat{\nabla}\rho$, one has

$$\hat{f} \simeq \hat{f}' + \tfrac{1}{2}m(1 + \lambda\Delta\hat{\rho})|\nabla\hat{\rho}|^2, \qquad (5)$$

where $\hat{f}' = \hat{f}'(\Delta\hat{\rho}, \Delta\hat{T})$ is the gradient-independent portion of $\hat{f}$, and λ is a dimensionless coupling parameter which contributes the correlation length asymmetry. Then, as shown by Cahn [10], $\mathbf{w} = m(1 + \lambda\Delta\hat{\rho})\nabla\hat{\rho}$. In the mean-field approximation, the asymmetric gradient contribution to the Helmholtz energy density $\lambda\Delta\hat{\rho}|\hat{\nabla}\hat{\rho}|^2 \sim \lambda(\Delta\hat{\rho})^3/\xi^2$ is of the same order, in terms of the temperature variable $|\Delta\hat{T}|$, as the two other leading asymmetric contributions $\sim\Delta\hat{T}(\Delta\hat{\rho})^3$ and $\sim(\Delta\hat{\rho})^5$ in the Landau expansion of $\hat{f}'$. Thus all three asymmetry contributions may be equally important.

It is known that the asymptotic critical behavior of the Ising model can be described by two scaling fields, h_1 (ordering field) and h_2 (thermal field), which are thermodynamically conjugate to two scaling densities, the strongly fluctuating order parameter ϕ_1, and the weakly fluctuating ϕ_2. A third field h_3 is the critical part of an appropriate thermodynamic potential [1,2]. In zero ordering field ($h_1 = 0$) below T_c in the bulk phases, where $\nabla\phi_1 = 0$, the order parameter is

$$\phi_1 = \left(\frac{\partial h_3}{\partial h_1}\right)_{h_2} \approx \pm\hat{B}_0|h_2|^\beta, \qquad (6)$$

where $\hat{B}_0$ is a critical amplitude.

Complete scaling for homogeneous fluids expresses the fields of the Ising model as functions of all three physical fields, via $h_{1,2,3} = h_{1,2,3}(\hat{P}, \hat{T}, \hat{\mu})$ [1]. When the Ising fields are expanded in powers of the physical fields, the lowest-order terms in the expansions, corresponding to the linear mixing of the physical fields, result in the leading asymmetry corrections in the thermodynamic properties [1,2]. Unlike the previously proposed treatment of fluid asymmetry, which generates an independent "asymmetry" exponent [11], complete scaling does not generate independent critical exponents; the power-law exponents of the asymmetric subsingularities are combinations of the Ising asymptotic critical exponents.

The extension of complete scaling to inhomogeneous systems that we propose is formulated as follows:

(1) In analogy with Eq. (4), the gradient of the order parameter $\nabla\phi_1$ and its conjugate field $\mathbf{h}_4$ are included in the Gibbs-Duhem relation for the symmetric Ising model, so that

$$dh_3 = \phi_1 dh_1 + \phi_2 dh_2 + \hat{\nabla}\phi_1 \cdot d\mathbf{h}_4. \qquad (7)$$

(2) The complete-scaling concept of field mixing is then extended to include the physical field $\hat{\mathbf{w}}$ conjugate to the

gradient of the physical density, and the Ising field $\mathbf{h}_4$. The lowest-order gradient-dependent contribution to the Ising fields is $|\hat{\mathbf{w}}|^2$. Thus the generalized complete-scaling equations become

$$h_1 = a_1\Delta\hat{\mu} + a_2\Delta\hat{T} + a_3\Delta\hat{P} + \tfrac{1}{2}a_4|\hat{\mathbf{w}}|^2, \qquad (8)$$

$$h_2 = b_1\Delta\hat{T} + b_2\Delta\hat{\mu} + b_3\Delta\hat{P} + \tfrac{1}{2}b_4|\hat{\mathbf{w}}|^2, \qquad (9)$$

$$h_3 = c_1\Delta\hat{P} + c_2\Delta\hat{\mu} + c_3\Delta\hat{T} + \tfrac{1}{2}c_4|\hat{\mathbf{w}}|^2, \qquad (10)$$

$$\mathbf{h}_4 = d_1\hat{\mathbf{w}}. \qquad (11)$$

The *leading* asymmetric corrections are captured by a simplified set of complete-scaling transformations [2]

$$h_1 = \Delta\hat{\mu} + a_3[\Delta\hat{P} - \hat{s}_c\Delta\hat{T}] + \tfrac{1}{2}a_4|\hat{\mathbf{w}}|^2, \qquad (12)$$

$$h_2 = \Delta\hat{T}, \qquad (13)$$

$$h_3 = \Delta\hat{P} - \hat{s}_c\Delta\hat{T} - \Delta\hat{\mu}, \qquad (14)$$

$$h_4 = \hat{\mathbf{w}}. \qquad (15)$$

Here, $\hat{s}_c$ corresponds to a specific choice of the critical-entropy density $\hat{s}_c = (d\hat{P}/d\hat{T})_{h_1=0,c}$, which is arbitrary in classical thermodynamics [2]. The coefficients a_1, b_1, c_1, and d_1, can be absorbed by a normalization of the scaling fields [2]. For the symmetric Ising or lattice-gas model $a_3 = a_4 = 0$. Equation (13) neglects the physical-field mixing in h_2. This particular mixing is responsible for the subleading singular contribution to the mean density of order $|\Delta\hat{T}|^{1-\alpha}$ [1,2]. While for some simple fluids the subleading term may be important if a_3 is particularly small, for highly asymmetric fluids, such as ionic liquids or fluids with large molecular volumes, the leading singular term always dominates [2–4,12]. The effects of the subleading singularities on the asymmetric interfacial profiles will be published elsewhere.

The physical densities are found in terms of the scaling densities by combining the Gibbs-Duhem relations given by Eqs. (4) and (7) with Eqs. (12)–(15). The resulting expressions, expanded to leading order in the asymmetric corrections, are

$$\Delta\hat{\rho} \simeq (1 + a_3)\phi_1 + a_3(1 + a_3)\phi_1^2, \qquad (16)$$

$$\hat{\nabla}\hat{\rho} \simeq [1 + (a_3 + a_4)\phi_1]\hat{\nabla}\phi_1. \qquad (17)$$

To make Eq. (17) consistent with Eq. (16), we must interpret Eq. (17) as describing a coordinate transformation. This transformation can be consistently formulated if the gradients are defined as follows:

$$\nabla\phi_1 \equiv \frac{\partial\phi_1(\mathbf{r}_s)}{\partial\mathbf{r}_s} \quad \text{and} \quad \nabla\hat{\rho} \equiv \frac{\partial\hat{\rho}(\mathbf{r}_a)}{\partial\mathbf{r}_a}, \qquad (18)$$

where $\mathbf{r}_s$ and $\mathbf{r}_a$ are position vectors which belong to two distinct coordinate systems for the Ising model and asymmetric physical variables, respectively. An explicit relationship between $\mathbf{r}_s$ and $\mathbf{r}_a$ is found by combining Eq. (18)

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with Eqs. (16) and (17) and integrating, which yields

$$\hat{\mathbf{r}}_s = \hat{\mathbf{r}}_a + (a_4 - a_3) \int_0^{\hat{\mathbf{r}}_a} \phi_1(\hat{\mathbf{r}}_a') d\hat{\mathbf{r}}_a', \qquad (19)$$

where $\hat{\mathbf{r}}_s = \mathbf{r}_s/2\xi_s$ and $\hat{\mathbf{r}}_a = \mathbf{r}_a/2\xi_s(1 + a_3)$ are normalized by the correlation length $\xi_s \approx \xi_0^- |\Delta\hat{T}|^{-\nu}$ of the symmetric system. Just as in asymmetric fluids where $\mathbf{w} = (1 + \lambda\Delta\hat{\rho})\hat{\nabla}\hat{\rho}$, the field $\mathbf{h}_4$ in the symmetric system is related to $\hat{\nabla}\phi_1$ by $\mathbf{h}_4 = \hat{\nabla}\phi_1$. This condition, together with Eqs. (15) and (17), constrains the relationship between the mixing coefficients:

$$a_4 = -a_3 - (1 + a_3)\lambda. \qquad (20)$$

Thus even if $\lambda = 0$, complete scaling induces a coordinate transformation [cf. Eq. (19)]. It is important to note that, while the critical fluctuations strongly affect the behavior of the scaling and, consequently, physical variables, the mixing coefficients are determined by short-range intermolecular forces and thus can be estimated from an appropriate mean-field equation of state [7].

As an application of the extended complete-scaling transformations, we calculate, through the known Ising-model order-parameter profile, the fluctuation-modified asymmetric density profile, which is difficult to derive otherwise. While the z direction is assigned by gravity, we ignore other effects of gravity [13]. The planar interfacial profile is determined by minimizing $\hat{f} - \hat{\mu}_\infty\hat{\rho}$, where $\hat{\mu}_\infty$ is the bulk chemical potential at phase coexistence [8]: $\partial(\hat{f} - \hat{\mu}_\infty\hat{\rho})/\partial\hat{\rho} = 0$. Multiplying this expression by $\hat{\nabla}\hat{\rho}$, integrating, and using Eq. (5), we see that

$$\hat{f}' - \hat{\mu}_\infty\hat{\rho} = \tfrac{1}{2}\hat{\mathbf{w}} \cdot \hat{\nabla}\hat{\rho}. \qquad (21)$$

By inverting the complete-scaling transformations, we can reexpress Eq. (21) in terms of the symmetric Ising variables, leading to

$$(1 - a_4\phi_1)[h_1'\phi_1 - h_3' + h_{3,\infty}] = \tfrac{1}{2}\mathbf{h}_4 \cdot \hat{\nabla}\phi_1, \qquad (22)$$

where h_1' and h_3' are the gradient-independent portions of h_1 and h_3.

The one-dimensional solution of Eq. (22) can be found perturbatively using the form $\phi_1 = \phi_1^{(0)} + a_4\phi_1^{(1)}$ and matching powers of a_4. The leading (symmetric) term is found by solving Eq. (22) with $a_4 = 0$:

$$\phi_1^{(0)}(\hat{z}_s) = \hat{B}_0|h_2|^\beta \Psi(\hat{z}_s). \qquad (23)$$

In the first-order-epsilon approximation ($\epsilon = 4 - d$ with d being the dimensionality) the antisymmetric function $\Psi(\hat{z}_s)$ reads [8,14,15]:

$$\Psi(\hat{z}_s) = \tanh(\hat{z}_s)\left[1 - \frac{\pi\epsilon}{6\sqrt{3}}\text{sech}^2(\hat{z}_s)\right]. \qquad (24)$$

The term $\phi_1^{(1)}$ is then given by

$$\phi_1^{(1)}(\hat{z}_s) = -\frac{1}{2}\partial_{\hat{z}_s}\phi_1^{(0)}(\hat{z}_s) \int_0^{\hat{z}_s} \phi_1^{(0)}(\hat{z}_s') d\hat{z}_s'. \qquad (25)$$

The solution $\phi_1(\hat{z}_s)$ can be rewritten in terms of the physi-
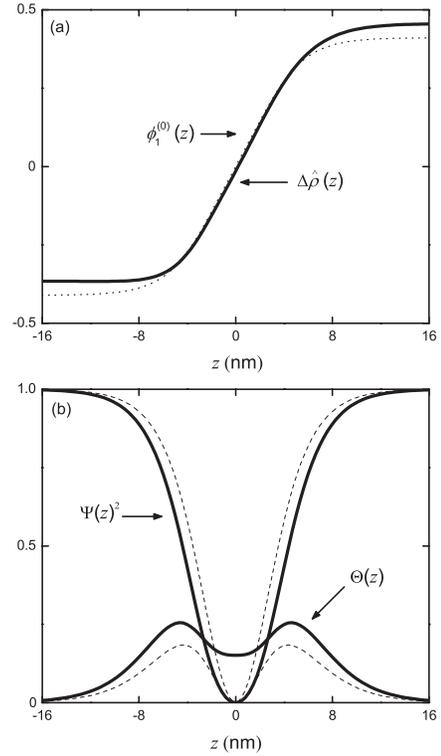
FIG. 1. (a) The density profile given by Eq. (27) (solid curve) and the symmetric profile by Eqs. (23) and (24) (dots), plotted for heptane at $|\Delta\hat{T}| = 0.01$ with $B_0 = 1.84$, $a_3 = 0.37$, $\xi_0^- = 0.11$ nm [2], and assuming $\lambda = a_3$. (b) The profile functions $\Psi^2(z)$ and $\Theta(z)$ evaluated for heptane (solid curves). The mean-field ($\epsilon = 0$) results are shown as dashed curves.

cal coordinate system with the transformation given by Eq. (19). After expanding to leading order in the asymmetry, we find

$$\phi_1(\hat{z}_s) \simeq \phi_1^{(0)}(\hat{z}_a) + \left(\frac{1}{2}a_4 - a_3\right)\partial_{\hat{z}_a}\phi_1^{(0)} \int \phi_1^{(0)}(\hat{z}_a') d\hat{z}_a'. \qquad (26)$$

The complete expression for the planar physical density profile is found by combining Eq. (26) with the complete-scaling expression for the density given by Eq. (16):

$$\Delta\hat{\rho}(\hat{z}_a) \simeq B_0|\Delta\hat{T}|^\beta \Psi(\hat{z}_a) + D|\Delta\hat{T}|^{2\beta}\Psi^2(\hat{z}_a)$$
$$- \tfrac{3}{2}[D + D_\lambda]|\Delta\hat{T}|^{2\beta}\Theta(\hat{z}_a), \qquad (27)$$

where $\Theta \equiv \partial_{\hat{z}_a}\Psi(\hat{z}_a) \int \Psi(\hat{z}_a') d\hat{z}_a'$, $B_0 = (1 + a_3)\hat{B}_0$, $D = a_3 B_0^2/(1 + a_3)$, and $D_\lambda = 1/3 B_0^2\lambda$. The derived profile exhibits the correct limiting behavior in the mean-field limit ($\epsilon = 0$), where it reproduces the result obtained by Fisher (M. A.) and Wortis [16] in the $\lambda = 0$ approximation, and in the fluctuation-modified symmetric limit ($a_3 = a_4 = \lambda = 0$), where it reduces to $\phi_1^{(0)}(\hat{z}_s)$. The derived density profile near the critical point for heptane is compared with the density profile of a symmetric system in Fig. 1(a) and with the asymmetric mean-field profile in Fig. 1(b). Since $\Psi^2(\hat{z}_s \to \pm\infty) = 1$, the second term in

Eq. (27) generates the leading contribution to the non-analytic mean density in the bulk phases given by Eq. (1). In contrast, because $\Theta(\hat{z}_s \to \pm\infty) = 0$, the third term contributes to the density profile only in the vicinity of the interface and is responsible for the value of Tolman's length.

While the asymptotic planar surface tension [8,14] remains essentially unaltered by the inclusion of fluid asymmetry, Tolman's length, is entirely dependent on the asymmetry. A general expression for Tolman's length in terms of the planar interfacial profile was obtained by Fisher and Wortis [16] in the square-gradient theory. They found

$$\delta = \frac{\int z \partial_z \hat{\rho}}{\int \partial_z \hat{\rho}} - \frac{\int z [\partial_z \hat{\rho}]^2}{\int [\partial_z \hat{\rho}]^2}, \qquad (28)$$

where all integrals are taken from $z = -\infty$ to $z = \infty$. By substituting Eq. (27) into Eq. (28), we have explicitly calculated the leading singular contribution to Tolman's length in the first-order epsilon approximation:

$$\delta \approx -\frac{5}{4}\left(1 + \frac{4\pi\epsilon}{375\sqrt{3}}\right)\frac{[D + D'_\lambda]\xi_0^-}{B_0}|\Delta\hat{T}|^{\beta-\nu}, \qquad (29)$$

where $D'_\lambda = (1 + 8\pi\epsilon/75\sqrt{3})D_\lambda$. In the mean-field limit, where the leading term $\propto |\Delta\hat{T}|^{2\beta}$ and the subleading singularity $\propto |\Delta\hat{T}|^{1-\alpha}$ collapse into $\propto |\Delta\hat{T}|$, Eq. (29) exactly reproduces the previously reported results [16,17], but only with $\lambda = 0$. The phenomenological expression (3) also agrees asymptotically with Eq. (29) if $\lambda = 0$ and the prefactor is absorbed in the definition of the interfacial width.

If we write $\delta \approx \delta_0 |\Delta\hat{T}|^{\beta-\nu}$, Eq. (29) with $\lambda = 0$ suggests a new universal ratio between critical amplitudes, namely,

$$-\frac{\delta_0 B_0}{D\xi_0^-} \simeq 1.27 \qquad (\epsilon = 1). \qquad (30)$$

However, if $\lambda \neq 0$, the existence of $D'_\lambda \propto \lambda$ breaks this universality. Physically, the asymmetric gradient-term coefficient λ may be associated with three-body interactions, which generate a term $\sim \rho^3$ in a mean-field equation of state. As there is no such term in the van der Waals equation of state, D_λ vanishes for a van der Waals fluid. Unlike a_3, which determines the singularity in the mean density, the asymmetric gradient coefficient λ cannot be found from bulk-fluid phase behavior. Consequently, any purely thermodynamic expressions for Tolman's length are incomplete.

The significance of the gradient asymmetry has not been previously discussed in the literature. It can be shown that λ contributes to the asymmetry of the correlation length,

$$\xi^2 \simeq \xi_s^2\left[1 \pm \left(\frac{3a_3}{1 + a_3} + \lambda\right)B_0|\Delta\hat{T}|^{\beta}\right], \qquad (31)$$

where the part containing a_3 originates from asymmetry in the thermodynamic susceptibility, while λ, which we expect to be of the same order of magnitude as a_3, comes

from asymmetry in the density gradient, as given by Eq. (5). By measuring the susceptibilities (in the zero wave-number limit) and the correlation lengths in lighter and denser coexisting fluid phases by light scattering, one can obtain a_3 and λ independently and thus calculate the Tolman-length amplitude δ_0.

Complete scaling of spatially nonuniform fluids can be further extended to include interfaces in fluid mixtures. Bulk thermodynamic behavior of binary fluids is covered by conventional complete scaling where four physical fields are equally mixed into three symmetric Ising scaling fields [3,4]. Consequently, both density and concentration inhomogeneities should be incorporated into the scaling fields. Other possible applications of the proposed approach go beyond interfacial inhomogeneities in fluids. Complete scaling can also be extended to the description of near-critical fluids in external fields, such as the electric field [18].

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