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Nature of vapor-liquid asymmetry in fluid criticality

Jingtao Wang and Mikhail A. Anisimov*
Department of Chemical and Biomolecular Engineering and Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742, USA

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We have investigated the nature and experimental consequences of vapor-liquid asymmetry in near-critical fluids within the framework of "complete scaling" [M. E. Fisher and G. Orkoulas, Phys. Rev. Lett. **85**, 696 (2000); Y. C. Kim *et al.*, Phys. Rev. E **67**, 061506 (2003)]. We used the thermodynamic freedom for a choice of the critical-entropy value to simplify "complete scaling" to a form with only two independent parameters, responsible for two different sources of the asymmetry. We then developed a procedure to obtain these two parameters from mean-field equations of state. By combining accurate liquid-vapor coexistence and heat-capacity data, we have unambiguously separated two nonanalytic contributions from the two sources of vapor-liquid asymmetry and proved the validity of "complete scaling." Since the nonanalytic asymmetry effects in the critical region are fully determined by the Ising critical exponents for the symmetric lattice-gas model, there is no need for a special renormalization-group theoretical treatment of "non-Ising" asymmetry in fluid criticality.

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I. INTRODUCTION

An appropriate choice of the order parameter is necessary to describe critical phenomena in fluids in terms of the general theory of phase transitions [1–4]. Thermodynamics itself does not specify uniquely which set of variables is to be used in describing critical behavior of real fluids and the choice is commonly based on intuition, empirical considerations, or made by comparison with a microscopic model.

The simplest and most important model to illuminate the physics of critical phenomena in fluids is the lattice-gas model. The lattice gas, which is a translation of the Ising model to fluids [5], has perfect symmetry with respect to the density ρ, exhibiting a symmetric vapor-liquid coexistence curve [6]. Hence, in the lattice gas, the arithmetic mean of the liquid and vapor densities, the "diameter" of the coexistence curve, is a vertical straight line. The order parameter in the lattice gas is $\Delta\hat{\rho}=(\rho-\rho_c)/\rho_c$, where ρ_c is the critical value of the molecular density. However, in real fluids the arithmetic mean of the liquid and vapor densities, which may look approximately as a straight line, known as the rectilinear diameter, generally, does not coincide with the critical isochore $\rho=\rho_c$.

It has been over 100 years since the "law" of the rectilinear diameter was first proposed by Cailletet and Mathias [7]. The "law" states that the mean of the liquid and vapor densities, ρ' and ρ'', is a linear function of the temperature T,

$$\hat{\rho}_d=\frac{\rho'+\rho''}{2\rho_c}=1+D|\Delta\hat{T}|, \tag{1}$$

where the coefficient D is the slope of the rectilinear diameter, $\Delta\hat{T}=(T-T_c)/T_c$ with T_c being the critical temperature. While extrapolation of the rectilinear diameter to the critical temperature is commonly used to obtain the critical density, such a procedure may lead to a significant error, as shown in Fig. 1. Some fluids, such as oxygen [8] (see also Ref. [6]) and xenon [9], indeed follow the "law" of the rectilinear diameter within the experimental accuracy. Moreover, the "diameter," accurately obtained by Hahn *et al.* [10] for ^{3}He very close to the critical point, is a straight line with an almost zero slope; incidentally, this symmetry goes far beyond the range of the Ising-model asymptotic power law. However, some fluids such as sulfur hexafluoride (SF_6) [11] and trifluorotrichloroethane ($C_2F_3Cl_3$, Freon-113) [12] have been found to exhibit strong deviations from the "law" of the rectilinear diameter. In particular, the data on SF_6 were considered as the first reliable experimental evidence of a "singular diameter" in fluids [13]. The "diameters" for several fluids are shown in Fig. 2. A striking difference between such fluids as SF_6 and Freon-113 on the one hand and nitrogen and neon [14] on the other hand is puzzling. Indeed, the concept of the rectilinear diameter is essentially mean field. Any classical equation of state, such as the van der Waals

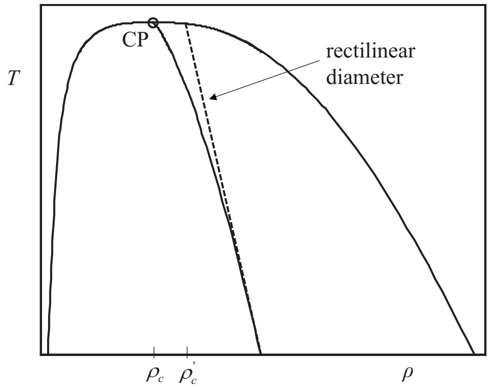

FIG. 1. Schematic illustration of a liquid-vapor coexistence curve. Dashed line is the rectilinear diameter; ρ_c' is the critical density extrapolated with the rectilinear diameter; ρ_c is the actual critical density. The critical point (CP) is indicated by the circle.

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*Author to whom correspondence should be addressed. Electronic address: anisimov@umd.edu.

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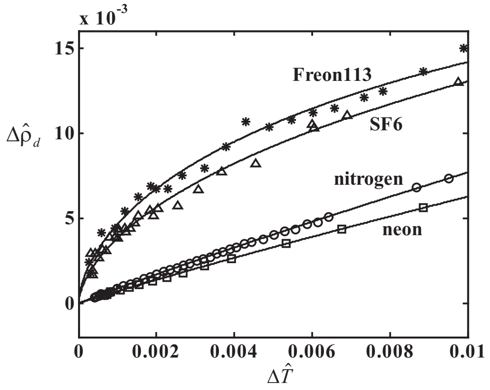

FIG. 2. “Diameters” of vapor-liquid coexistence for several fluids. Experimental data for Freon-113 [12] and for SF$_6$, nitrogen and neon [14] are represented by symbols; solid curves are fits to Eq. (45).

equation, yields asymptotically a rectilinear diameter near the critical point. However, how can the rectilinear diameter persist in some real fluids, which all exhibit the universal nonanalytic (scaling) shape of the phase boundary?

A few theoretical models for the description of the “singular diameters” have been developed since the early 1970s. These models, such as Mermin’s decorated lattice-gas model [15] and Widom-Rowlinson’s penetrable-sphere model [6,16], all yield a slope of the “diameter” diverging at the critical point as the heat capacity at constant volume C_V,

$$\frac{d\rho_d}{dT} \propto \frac{C_V}{k_B} \approx A_0^-|\Delta\hat{T}|^{-\alpha}, \tag{2}$$

where k_B is Boltzmann’s constant, $\alpha \simeq 0.109$ is an Ising universal critical exponent [17,18], A_0^- is a system-dependent amplitude for the heat-capacity asymptotic power law in the two-phase region. (Here and below the symbol $\simeq$ means approximately equal, while the symbol $\approx$ means asymptotically equal.) Therefore, the “diameter” is expected to contain a nonanalytic term $\propto|\Delta\hat{T}|^{1-\alpha}$,

$$\hat{\rho}_d = 1 + D_1|\Delta\hat{T}|^{1-\alpha} + D_0|\Delta\hat{T}| + \cdots. \tag{3}$$

However, a more general formulation of fluid criticality, suggested recently by Fisher and co-workers [19–21] and known as “complete scaling,” yields a more significant additional nonanalytic term in the “diameter,” namely, $\propto|\Delta\hat{T}|^{2\beta}$ with $\beta \simeq 0.326$ [17,18], so that

$$\hat{\rho}_d = 1 + D_2|\Delta\hat{T}|^{2\beta} + D_1|\Delta\hat{T}|^{1-\alpha} + D_0|\Delta\hat{T}| + \cdots. \tag{4}$$

The first nonanalytic term in Eq. (4), $\propto|\Delta\hat{T}|^{2\beta}$, dominates near the critical point since $2\beta < 1-\alpha$. The question arises: is this term, or either of the two predicted nonanalytic terms, experimentally detectable?

First of all, the exact form or even the existence of nonanalytic terms in the “diameter” of real fluids has never been detected unambiguously. While some fluids show strong deviations from a rectilinear diameter [14], many fluids show very little or no deviations at all [6,9,14]. What is the physical reason for the apparently so different asymmetry in phase behavior of the different fluids?

Pestak *et al.* [14] studied experimental data for “diameters” of several fluids in 1987. They concluded that the slope of the rectilinear diameter far away from the critical point and the amplitude of deviations from the rectilinear diameter within the critical region are both proportional to the product of molecular polarizability and density, which is a measure of the relative significance of three-body interactions. However, after reanalyzing the same data and including additional fluid systems in the study, Singh and Pitzer [22] found that the diameter slope shows a linear dependence on the acentric factor and concluded that the shape of the pair intermolecular potential should be the primary factor in the slope of the diameter (at least, far away from the critical point) rather than the relative strength of three-body interactions. They also speculated that closer to the critical point the shape of the two-body potential might have a similar effect on the increase of the amplitude D_1 in the nonanalytic term of Eq. (3). At that time, the existence of the more significant $|\Delta\hat{T}|^{2\beta}$ term present in Eq. (4) was not known.

In this paper we study the physical nature and experimental consequences of vapor-liquid asymmetry in near-critical fluids within the framework of “complete scaling” originally formulated by Fisher and co-workers [19–21]. Some principal results of our study have been presented in Ref. [23]. By combining accurate liquid-vapor coexistence and heat-capacity data, we have unambiguously separated two nonanalytic contributions to vapor-liquid asymmetry and proved the validity of “complete scaling.” We have shown that in fluids there are two sources of vapor-liquid asymmetry, one associated with a coupling between the symmetric order parameter and entropy and another one associated with a coupling between the order parameter and volume per molecule. We have developed a thermodynamic procedure to obtain two parameters, responsible for these two sources of asymmetry, from mean-field equations of state. We have also demonstrated, with the help of crossover theory [4], how the rectilinear diameter splits into two nonanalytic terms near the critical point.

In addition to the nonanalytic asymmetry in the vapor-liquid coexistence, “complete scaling” explains the so-called Yang-Yang anomaly [24] and the divergence of the Tolman length near the critical point [25]. The concept of “non-Ising asymmetry” in fluids was intensively explored by theoretical physicists in the 1980s [26–28,30–32]. However, since the asymmetry in fluid criticality are fully determined by the Ising critical exponents for the symmetric lattice-gas model, the effects of “non-Ising asymmetry” have no practical relevance.

II. FISHER’S “COMPLETE SCALING”

For one-component fluids, the critical point is specified by the critical temperature T_c, critical density ρ_c, and critical pressure P_c. The thermodynamic properties reduced by the critical parameters are defined as follows:

$$\hat{T}=\frac{T}{T_c},\quad \hat{\rho}=\frac{\rho}{\rho_c},\quad \hat{P}=\frac{P}{\rho_c k_B T_c},$$

$$\hat{\mu}=\frac{\mu}{k_B T_c},\quad \hat{A}=\frac{A}{k_B T_c},\quad \hat{S}=\frac{S}{k_B},$$

$$\hat{C}_V=\frac{C_V}{k_B},\quad \hat{\chi}=\left(\frac{\partial^2\hat{P}}{\partial\hat{\mu}^2}\right)_{\hat{T}}=\left(\frac{\partial\hat{\rho}}{\partial\hat{\mu}}\right)_{\hat{T}}, \tag{5}$$

where μ is the chemical potential (Gibbs energy per molecule), P is the pressure, S is the entropy per molecule, C_V is the isochoric heat capacity per molecule, A is the Helmholtz energy per molecule, and $\hat{\chi}$ is the isothermal susceptibility.

It is commonly accepted that the nonanalytic critical behavior of real fluids and fluids mixtures can be asymptotically described by scaling theory in terms of two independent scaling fields, namely, h_1 (“ordering” field) and h_2 (“thermal” field) and two conjugate scaling densities, namely, the order parameter ϕ_1 (strongly fluctuating) and ϕ_2 (weakly fluctuating). The third field, h_3 is the critical part, which exhibits minimum with respect to a variation of the order parameter, of an appropriate field-dependent thermodynamic potential, such that

$$dh_3=\phi_1 dh_1+\phi_2 dh_2. \tag{6}$$

In scaling theory the thermodynamic potential h_3 is a homogeneous function of h_1 and h_2. Asymptotically,

$$h_3\approx|h_2|^{2-\alpha}f^{\pm}\left(\frac{h_1}{|h_2|^{2-\alpha-\beta}}\right), \tag{7}$$

where $f^{\pm}$ is a scaling function and the superscript ± refers to $h_2>0$ and $h_2<0$, respectively. The form of the scaling function is universal; however, it contains two thermodynamically independent (but system-dependent) amplitudes. All other asymptotic amplitudes are related to the selected ones by universal relations. The critical exponents α and β are universal within a class of critical-point universality. All fluids and fluid mixtures belong to the Ising-model class of universality (in which the order parameter is either a scalar or a one-component vector) [1]. The Ising values for α and β, given in the Introduction, are well established theoretically and confirmed experimentally [1–4,17,18]. The two Ising amplitudes, $\hat{A}_0$ and $\hat{B}_0$ can be determined by the asymptotic power-law behavior of the two scaling densities in zero ordering field ($h_1=0$),

$$\phi_1=\left(\frac{\partial h_3}{\partial h_1}\right)_{h_2}\approx\pm\hat{B}_0|h_2|^{\beta}, \tag{8}$$

$$\phi_2=\left(\frac{\partial h_3}{\partial h_2}\right)_{h_1}\approx\frac{\hat{A}_0^{\pm}}{1-\alpha}h_2|h_2|^{-\alpha}, \tag{9}$$

and of the three scaling susceptibilities, “strong” χ_1, “weak” χ_2, and “cross” χ_{12} in zero ordering field,

$$\chi_1=\left(\frac{\partial\phi_1}{\partial h_1}\right)_{h_2}\approx\hat{\Gamma}_0^{\pm}|h_2|^{-\gamma}, \tag{10}$$

$$\chi_2=\left(\frac{\partial\phi_2}{\partial h_2}\right)_{h_1}\approx\hat{A}_0^{\pm}|h_2|^{-\alpha}, \tag{11}$$

$$\chi_{12}=\left(\frac{\partial\phi_1}{\partial h_2}\right)_{h_1}\approx\beta\hat{B}_0\frac{|h_2|^{\beta}}{h_2}\quad(h_2<0), \tag{12}$$

where the critical exponent $\gamma=2-\alpha-2\beta\simeq1.239$ [17,18] and the other Ising critical amplitude $\hat{\Gamma}_0^{\pm}$ is related to $\hat{B}_0$ and $\hat{A}_0^{\pm}$ through universal ratios, $\alpha\hat{\Gamma}_0^{+}\hat{A}_0^{+}/\hat{B}_0^{2}\simeq0.0581$, $\hat{\Gamma}_0^{+}/\hat{\Gamma}_0^{-}\simeq4.8$, and $\hat{A}_0^{+}/\hat{A}_0^{-}\simeq0.523$ [18]. While the superscript ± refers to the states at $h_2>0$ and $h_2<0$, the prefactor ± in Eq. (8) refers to the branches of the order parameter at $h_1>0$ and $h_1<0$ sides, respectively.

In mean-field approximation, with $\alpha=0$ and $\beta=1/2$, Eq. (7) reduces to the asymptotic Landau expansion [29],

$$-h_3\approx\tfrac{1}{2}a_0h_2\phi_1^2+\tfrac{1}{24}u_0\phi_1^4-h_1\phi_1, \tag{13}$$

where a_0 and u_0 are mean-field system-dependent amplitudes.

In the lattice-gas model $h_1=\Delta\hat{\mu}=(\mu-\mu_c)/k_BT_c$, $h_2=\Delta\hat{T}$, $\phi_1=\Delta\hat{\rho}$, and $\phi_2=\Delta(\hat{\rho}\hat{S})$, while $-h_3$ is the critical part of the grand thermodynamic potential $\Omega=-PV$ per unit volume V, so that $h_3=(P-P_{\mathrm{cxc}})/\rho_ck_BT_c$, where P_{cxc} is the pressure along the vapor-liquid coexistence which coincides with the condition $h_1=0$.

The lattice gas has perfect symmetry with respect to the sign of the order parameter, whereas real fluids approach such symmetry only asymptotically. To incorporate fluid asymmetry into the scaling theory, in 1970s Mermin and Rehr [33] and Patashinskii and Pokrovskii [34] introduced the concept of mixing the independent physical fields into the theoretical scaling fields (see also Refs. [35–37]). According to their approach, which we will call “incomplete scaling,” the independent scaling fields in fluids are linear combinations of chemical potential and temperature,

$$h_1=a_1\Delta\hat{\mu}+a_2\Delta\hat{T},\quad h_2=b_1\Delta\hat{T}+b_2\Delta\hat{\mu}, \tag{14}$$

while the dependent field $h_3=c_1\Delta\hat{P}+c_2\Delta\hat{T}$. Since any two independent critical amplitudes can be incorporated into the scaling function $f^{\pm}$, it is convenient to adopt $a_1=1$ and $b_1=1$; then $c_1=1$ while c_2 becomes $-(\partial\hat{P}/\partial\hat{T})_{h_1=0}$ taken at the critical point. Therefore, the critical part of the field-dependent thermodynamic potential remains the same as in the lattice gas, since in linear approximation $(P-P_{\mathrm{cxc}})/\rho_ck_BT_c=\Delta\hat{P}-(\partial\hat{P}/\partial\hat{T})_{h_1=0,c}\Delta\hat{T}$. Furthermore, as shown by Anisimov *et al.* [36,37], since in classical thermodynamics the absolute value of entropy is arbitrary, the critical value of entropy can be chosen upon practical convenience. It is seen clearly from the basic thermodynamic relation

$$dP=\rho d\mu+\rho SdT, \tag{15}$$

that, if the critical entropy is adopted as $S_c=\rho_c^{-1}(\partial P/\partial T)_{h_1=0,c}$, the coefficient a_2 in Eq. (14) vanishes and in linear approximation the chemical potential along the vapor-liquid coexistence does not depend on temperature. However, the curvature of this dependence, determined by the second derivative, is well defined. With this choice of the critical entropy, the mixing term $b_2\Delta\hat{\mu}$ in "incomplete scaling" becomes also well defined, being in lowest approximation the sole contribution to the vapor-liquid asymmetry in real fluids. In particular, since $\Delta\hat{\rho}=\phi_1+b_2\phi_2=\phi_1+b_2\Delta(\hat{\rho}\hat{S})$, this term explains the $|\Delta\hat{T}|^{1-\alpha}$ singularity in the "diameter" of the vapor-liquid coexistence curve given by Eq. (3), yielding $D_1=b_2\hat{A}_0^-/(1-\alpha)$. Mapping the asymmetric fluid criticality into the symmetric lattice model is achieved in "incomplete scaling" by a redefinition of the order parameter as $\phi_1=\Delta\hat{\rho}-b_2\Delta(\hat{\rho}\hat{S})$. In "incomplete scaling" the chemical potential μ (up to the third derivative [4]) is an analytic function of temperature along the vapor-liquid coexistence boundary and along the critical isochore above the critical point ($h_1=0$). Like in the lattice gas, the second derivative $(\partial^2\mu/\partial T^2)_{h_1=0}=(d^2\mu/dT^2)_{\text{cxc}}$ remains finite at the critical temperature T_c, while $(\partial^2 P/\partial T^2)_{h_1=0}=(d^2P/dT^2)_{\text{cxc}}$ diverges proportionally to the isochoric heat capacity $\hat{C}_V$.

At this point we encounter a major conceptual problem with mapping real fluids into the lattice gas even at the mean-field level. In the mean-field approximation the critical part h_3 of the thermodynamic potential, is represented by Landau expansion (13). When $h_1=\Delta\hat{\mu}, h_2=\Delta\hat{T}+b_2\Delta\hat{\mu}$, and $\phi_1=\Delta\hat{\rho}-b_2\Delta(\hat{\rho}\hat{S})$, this expansion generates asymmetric terms $\propto b_2\Delta\hat{T}(\Delta\hat{\rho})^3$ and $\propto b_2(\Delta\hat{\rho})^5$. However, in the simplest equation of state that realistically describes fluid phase behavior, the van der Waals equation, the term $\propto\Delta\hat{T}(\Delta\hat{\rho})^3$ is absent, while the term $\propto(\Delta\hat{\rho})^5$ exists. Furthermore, in most classical equations of state, $d\hat{\mu}^2/d\hat{T}^2$ along the liquid-vapor coexistence exhibits a discontinuity directly related to the existence of the independent fifth-order term in Landau expansion. The existence of the independent fifth-order term makes exact mapping of fluids into the lattice-gas model by the conventional mixing of physical fields impossible. This problem was recognized a long time ago [2] but was not clearly articulated. On the other hand, a theoretical renormalization-group treatment of the fifth-order term [26–28,30,31] resulted in the emergence of an independent critical exponent $\theta_5\simeq 1.3$ [32]. The exponent θ_5 does not exist in symmetric models and is expected to belong exclusively to fluids.

More recently, "incomplete scaling" was challenged by Fisher and co-workers [19,20] who developed a new approach, known as "complete scaling for fluids." They proposed that both $(\partial^2\mu/\partial T^2)_{h_1=0}$ and $(\partial^2 P/\partial T^2)_{h_1=0}$ diverge at the critical point like the isochoric heat capacity. A principal possibility of this effect has been known as the "Yang-Yang anomaly" [24] and has been a subject of discussions for decades [39]. The major conceptual result of "complete scaling," which we will explore in this paper, is that asymmetric fluids can be consistently mapped into the symmetric Ising criticality by appropriate mixing of the physical fields into the scaling fields. Moreover, we argue in this paper that a redefinition of the order parameter, suggested by "complete scaling," makes a special renormalization-group treatment of the fifth-order term in the effective Hamiltonian for fluids irrelevant, at least, in practice.

"Complete scaling" suggests that all three physical fields $\Delta\hat{\mu}, \Delta\hat{T}$, and $\Delta\hat{P}$ are equally mixed into three scaling fields h_1, h_2, and h_3. In linear approximation

$$h_1 = a_1\Delta\hat{\mu} + a_2\Delta\hat{T} + a_3\Delta\hat{P}, \tag{16}$$

$$h_2 = b_1\Delta\hat{T} + b_2\Delta\hat{\mu} + b_3\Delta\hat{P}, \tag{17}$$

$$h_3 = c_1\Delta\hat{P} + c_2\Delta\hat{\mu} + c_3\Delta\hat{T}. \tag{18}$$

The dependent field h_3 is a homogeneous function of h_1 and h_2 as asymptotically given by Eq. (7). Far away from the asymptotic region, or if the phase-coexistence locus $h_1=0$ exhibits a strong curvature in terms of the physical fields [40], the linear approximation might be insufficient and appropriate nonlinear terms should be included.

Physical density-like properties, the molecular density and entropy per unit volume, are given by the thermodynamic relations

$$\hat{\rho} = \left(\frac{\partial\hat{P}}{\partial\hat{\mu}}\right)_{\hat{T}}, \quad \hat{\rho}\hat{S} = \left(\frac{\partial\hat{P}}{\partial\hat{T}}\right)_{\hat{\mu}}. \tag{19}$$

Since the coefficients c_1 and c_2 can be absorbed by making the thermodynamic potential h_3 dimensional, as given by Eq. (5), while the coefficient $c_3=\hat{S}_c$, one can obtain by applying Eq. (19) to Eqs. (16)–(18),

$$\hat{\rho} = \frac{1 + a_1\phi_1 + b_2\phi_2}{1 - a_3\phi_1 - b_3\phi_2}, \tag{20}$$

$$\hat{\rho}\hat{S} = \frac{\hat{S}_c + a_2\phi_1 + b_1\phi_2}{1 - a_3\phi_1 - b_3\phi_2}. \tag{21}$$

One can see that while the scaling fields are expressed as linear combinations of the physical fields, the physical densities are nonlinear combinations of the scaling densities.

III. MAKING "COMPLETE SCALING" SIMPLE

Before we apply complete scaling to describe asymmetry in fluids, we note that the relations between scaling and physical fields can be further simplified. The coefficients a_1 and b_1 can be absorbed by the two amplitudes in the scaling function $f^{\pm}$, such that $a_1=1$ and $b_1=1$. The coefficient $c_3=\hat{S}_c$ is determined by the choice of the critical value of entropy. By adopting $\hat{S}_c=(k_B\rho_c)^{-1}(\partial P/\partial T)_{h_1=0,c}=(d\hat{P}/d\hat{T})_{\text{cxc},c}$, the slope of the saturation-pressure curve at the critical point, one obtains $a_2=-a_3(d\hat{P}/d\hat{T})_{\text{cxc},c}$. Indeed, along the path $h_1=0$, asymptotically close to the critical point

$$\left(\frac{\partial\hat{\mu}}{\partial\hat{T}}\right)_{h_1=0,c} + a_2 + a_3\left(\frac{\partial\hat{P}}{\partial\hat{T}}\right)_{h_1=0,c} = 0. \tag{22}$$

On the other hand, it follows from the thermodynamic relation (15) that

$$\frac{d\hat{\mu}}{d\hat{T}}+\hat{S}_c-\frac{\partial\hat{P}}{\partial\hat{T}}=0. \tag{23}$$

Thus, with adopting $\hat{S}_c=(\partial\hat{P}/\partial\hat{T})_{h_1=0,c}$, we obtain $(\partial\hat{\mu}/\partial\hat{T})_{h_1=0,c}=0$ and

$$a_2+a_3\left(\frac{\partial\hat{P}}{\partial\hat{T}}\right)_{h_1=0,c}=0. \tag{24}$$

Furthermore, with such a choice of $\hat{S}_c$, along the path $h_1=0$,

$$h_2=\Delta\hat{T}\left(1-b_3\frac{a_2}{a_3}\right), \tag{25}$$

and the density of entropy becomes proportional to the weakly fluctuating scaling density, $\Delta(\hat{\rho}\hat{S})\approx(1+b_3)\phi_2 \propto|h_2|^{1-\alpha}$. With exception for a trivial renormalization of the amplitudes in h_2 and $\Delta(\hat{\rho}\hat{S})$, the coefficient b_3 plays no significant role in asymmetry of fluid criticality. Indeed, as follows from Eqs. (20) and (21), this coefficient can be independently obtained only from the contributions to the density behavior of order $b_3\phi_1\phi_2\propto|h_2|^{1-\alpha+\beta}$. With $1-\alpha+\beta\simeq1.417$, this contribution is of higher order than $a_3\phi_1^2\propto|h_2|^{2\beta}$ and $b_2\phi_2\propto|h_2|^{1-\alpha}$, and even significantly weaker than the linear term. Therefore, for the sake of simplicity, we assume $b_3=0$. Hence, there are only two independent coefficients that in the first approximation control the asymmetry in fluid criticality, namely a_3 and b_2. In this approximation, the scaling fields read

$$h_1=\Delta\hat{\mu}+a_3[\Delta\hat{P}-(d\hat{P}/d\hat{T})_{\text{cxc},c}\Delta\hat{T}], \tag{26}$$

$$h_2=\Delta\hat{T}+b_2\Delta\hat{\mu}, \tag{27}$$

$$h_3=\Delta\hat{P}-\Delta\hat{\mu}+(d\hat{P}/d\hat{T})_{\text{cxc},c}\Delta\hat{T}. \tag{28}$$

Furthermore, by expanding Eqs. (20) and (21) and neglecting all terms of higher order than linear of $\Delta\hat{T}$, we obtain

$$\Delta\hat{\rho}\simeq(1+a_3)\phi_1+a_3(1+a_3)\phi_1^2+b_2\phi_2, \tag{29}$$

$$\Delta(\hat{\rho}\hat{S})\simeq\phi_2. \tag{30}$$

As a result, while the order parameter in fluids is, in general, a nonlinear combination of density and entropy, the weakly fluctuating scaling density ϕ_2 in first approximation is associated with the density of entropy only.

IV. EXPERIMENTAL CONSEQUENCES OF "COMPLETE SCALING"

There are several important thermodynamic consequences of "complete scaling" that can be checked experimentally. First, the "diameter" of the vapor-liquid coexistence $\hat{\rho}_d$ should contain two major nonanalytical contributions, associated with the terms $a_3\Delta\hat{P}$ and $b_2\Delta\hat{\mu}$ in the scaling fields,

$$\begin{aligned}\hat{\rho}_d-1&=a_3(1+a_3)\phi_1^2+b_2\phi_2+\cdots\\&=D_2|\Delta\hat{T}|^{2\beta}+D_1|\Delta\hat{T}|^{1-\alpha}+D_0|\Delta\hat{T}|+\cdots,\end{aligned} \tag{31}$$

where, in accordance with Eqs. (8) and (9), $D_2=a_3B_0^2/(1+a_3)$ and $D_1=-b_2A_0^-/(1-\alpha)$ with B_0 and A_0^- being (experimentally determined) physical amplitudes in the asymptotic scaling power laws for the liquid-vapor densities, namely, $\Delta\hat{\rho}\approx\pm B_0|\Delta\hat{T}|^{\beta}$ and isochoric heat capacity in the two-phase region, $\hat{C}_V\approx A_0^-|\Delta\hat{T}|^{-\alpha}$. The simple relations between the Ising-model critical amplitudes $\hat{B}_0,\hat{A}_0^{\pm},\hat{\Gamma}_0^{\pm}$ and the physical amplitudes $B_0,A_0^{\pm},\Gamma_0^{\pm}$ (in the $b_3=0$ approximation) read

$$\hat{B}_0=\frac{B_0}{1+a_3},\quad \hat{A}_0^{\pm}=A_0^{\pm},\quad \hat{\Gamma}_0^{\pm}=\frac{\Gamma_0^{\pm}}{(1+a_3)^2}. \tag{32}$$

In "incomplete scaling" the Ising amplitudes and the physical amplitudes are identical.

Since $2\beta<1-\alpha$, the term $D_2|\Delta\hat{T}|^{2\beta}$ should dominate near the critical point. However, the apparent behavior of the "diameter" clearly depends on the magnitude of the complete-scaling mixing coefficient a_3. In practice, even close to the critical point, all three contributions in the "diameter" may be significant and statistically correlated. Attempts to fit some experimental and simulation data to Eq. (31) showed very poor conversions [41], mainly because of a strong correlation between the linear term $D_0|\Delta\hat{T}|$ and the nearly linear term $D_1|\Delta\hat{T}|^{1-\alpha}$.

Second, the presence of the $a_3\Delta\hat{P}$ term in h_1 implies the Yang-Yang anomaly: the divergence of the heat capacity in the two-phase region is shared among the second derivatives of pressure and chemical potential [19–21]. When applied to the two-phase coexistence at $\Delta\hat{T}<0$, the reduced form of the Yang-Yang relation [24] reads

$$\frac{\hat{\rho}\hat{C}_V}{\hat{T}}=\left(\frac{d^2\hat{P}}{d\hat{T}^2}\right)_{\text{cxc}}-\hat{\rho}\left(\frac{d^2\hat{\mu}}{d\hat{T}^2}\right)_{\text{cxc}}, \tag{33}$$

where $\hat{\rho}$ is the reduced overall density. In the lattice-gas model and in "incomplete scaling" $(d^2\hat{P}/d\hat{T}^2)_{\text{cxc}}$ diverges at the critical point such as the isochoric heat capacity, while $(d^2\hat{\mu}/d\hat{T}^2)_{\text{cxc}}$ remains finite. Contrarily, "complete scaling" at $\hat{\rho}=1$ yields [19,20],

$$\left(\frac{d^2\hat{\mu}}{d\hat{T}^2}\right)_{\text{cxc}}\approx-a_3\left(\frac{d^2\hat{P}}{d\hat{T}^2}\right)_{\text{cxc}}\approx-\frac{a_3}{1+a_3}\frac{\hat{C}_V}{\hat{T}}. \tag{34}$$

Therefore, the strength of the Yang-Yang "anomaly" is determined by the magnitude of the mixing coefficient a_3. Unfortunately, experimental tests of the Yang-Yang anomaly seem to be even more controversial than the attempts to separate the two singular terms in the "diameter" of the coexistence curve. Small traces of impurities can easily mimic such an anomaly, thus making any conclusions unreliable [42].

Another important consequence of complete scaling is a stronger asymmetry in the isothermal susceptibility than has been earlier predicted by "incomplete scaling." The total susceptibility $\hat{\chi}=(\partial\hat{\rho}/\partial\hat{\mu})_{\hat{T}}$, which contains two parts, symmetric

$\hat{\chi}_{\mathrm{sym}}$ and asymmetric $\hat{\chi}_{\mathrm{asym}}$, is, in general, a combination of three symmetric Ising susceptibilities, strong χ_1, weak χ_2, and cross χ_{12}, defined by Eqs. (10)–(12) [21,36]. A detailed derivation of the isothermal susceptibility, based on "complete-scaling," has been made by Kim *et al.* [21]. As a lower-order approximation of the result given in Ref. [21], one can obtain

$$\hat{\chi} = \left(\frac{\partial \hat{\rho}}{\partial \hat{\mu}}\right)_{\hat{T}} = \hat{\chi}_{\mathrm{sym}} + \hat{\chi}_{\mathrm{asym}} \simeq (1+a_3)^2\left(1 + \frac{3a_3}{1+a_3}\Delta\hat{\rho}\right)\chi_1 + b_2^2\chi_2 + 2(1+a_3)b_2\chi_{12}. \tag{35}$$

When $a_3=0$ ("incomplete" scaling), Eq. (35) becomes identical to the result earlier reported in Ref. [36].

By using expressions for the scaling susceptibilities along the vapor-liquid coexistence ($h_1=0$) given by Eqs. (10)–(12), one can derive from Eq. (35) [25]

$$\hat{\chi}_{\mathrm{sym}} \simeq \Gamma_0^-|\Delta\hat{T}|^{-\gamma}(1 + \Gamma_1^-|\Delta\hat{T}|^{\theta} + \cdots) \tag{36}$$

and

$$\hat{\chi}_{\mathrm{asym}} \simeq \pm\Gamma_0^-|\Delta\hat{T}|^{-\gamma}\left(\frac{3a_3}{1+a_3}B_0|\Delta\hat{T}|^{\beta} - 2b_2\frac{\beta B_0}{\Gamma_0^-}|\Delta\hat{T}|^{1-\alpha-\beta} + \cdots\right), \tag{37}$$

where Γ_1^- is the first (symmetric) correction amplitude, and $\theta \simeq 0.5$ is the "Wegner" correction exponent [43]. The combination $(\hat{\chi}' - \hat{\chi}'')/(\hat{\chi}' + \hat{\chi}'')$ asymptotically behaves as

$$\frac{\hat{\chi}' - \hat{\chi}''}{\hat{\chi}' + \hat{\chi}''} \approx \frac{3a_3}{1+a_3}B_0|\Delta\hat{T}|^{\beta} \tag{38}$$

$$- 2b_2\frac{\beta B_0}{\Gamma_0^-}|\Delta\hat{T}|^{1-\alpha-\beta}, \tag{39}$$

which, in principle, can be measured with static light scattering from the vapor and liquid coexisting phases. It contains, like the "diameter," two nonanalytic contributions with the first ("complete-scaling") term, $\propto|\Delta\hat{T}|^{\beta}$, dominating. No experiments have been so far performed to test "complete scaling" by light scattering.

Finally, the vapor-liquid asymmetry makes the surface tension σ to be dependent on the surface curvature, $1/R$, such that $\sigma=\sigma_\infty(1-2\delta/R)$ where σ_∞ is the surface tension for the planar interface. In perfectly symmetric systems, such as the lattice gas model or the "regular binary-solution" model, the surface tension does not depend on curvature. Most recently [25], it has been shown that Tolman's length δ, the curvature-correction coefficient in the surface tension, can be expressed through a ratio of the two parts of the susceptibility as

$$\frac{\delta}{\xi} \approx -\frac{\hat{\chi}_{\mathrm{asym}}}{2\hat{\chi}_{\mathrm{sym}}}, \tag{40}$$

where ξ is the correlation length of the density fluctuations in the two-phase region, in which ξ also serves as the thickness of the interface. The correlation length and/or thickness of the interface diverges asymptotically as

$$\xi \approx \xi_0^-|\Delta\hat{T}|^{-\nu}, \tag{41}$$

where ξ_0^- is the amplitude of the correlation length in the two-phase region and $\nu=(2-\alpha)/3 \simeq 0.630$ [18]. The amplitude ξ_0^- is related to ξ_0^+, the amplitude of the correlation length in the one-phase region, by a universal ratio $\xi_0^+ \simeq 1.96\xi_0^-$ [18]. By comparing Eqs. (36), (37), and (40), one can obtain that the Tolman length

$$\begin{aligned}\delta &\approx \mp\left(\frac{3a_3}{2(1+a_3)}B_0|\Delta\hat{T}|^{\beta-\nu} - b_2\frac{\beta B_0}{\Gamma_0^-}|\Delta\hat{T}|^{1-\alpha-\beta-\nu}\right)\xi_0^- \\ &\approx \mp\left(\frac{3a_3}{2(1+a_3)}\Delta\hat{\rho} + cb_2\frac{\Delta(\hat{\rho}\hat{S})}{\Delta\hat{\rho}}\right)\xi,\end{aligned} \tag{42}$$

where $\mp$ corresponds to a liquid droplet or a vapor droplet, respectively, $c=\beta B_0^2/\Gamma_0^- A_0^- \approx 1.58$, a universal amplitude ratio. The behavior of Tolman's length, given by Eq. (42), differs in an essential way from the results obtained within the framework of "incomplete scaling" [44–46]: a new term, $\propto|\Delta\hat{T}|^{\beta-\nu}$, emerges from the complete-scaling analysis. The first term in Eq. (42) diverges more strongly, since $\beta-\nu \simeq -0.304$, whereas $1-\alpha-\beta-\nu \simeq -0.065$. In "incomplete scaling," where $a_3=0$, Tolman's length diverges very weakly, namely as $|\Delta\hat{T}|^{1-\alpha-\beta-\nu}=|\Delta\hat{T}|^{-0.065}$ [44,45]. The divergence of Tolman's length predicted by "complete scaling" may be large enough to be detected in accurate experiments with microcapillaries and in simulations. No such experiments have been performed so far.

Overall, experimental verification of "complete scaling" is not simple. The nonanalytical contributions in the "diameter" are usually not large enough or/and strongly correlated with analytic terms. Moreover, the "incomplete scaling" result may be perfectly valid for some specific systems, such as the "penetrable sphere model" [16,44], since that model has an exact symmetry axis on which the chemical potential is an analytic function of temperature [47]. Therefore, the major question arises: does "complete scaling" have a solid experimental support?

V. "DIAMETERS" IN FLUIDS: SEPARATING TWO SOURCES OF ASYMMETRY

In this section we show the way to reliably determine the two asymmetry coefficients, a_3 and b_2, and to conclusively prove the validity of complete scaling by combining accurate experimental and simulation liquid-vapor coexistence with heat-capacity data. We have exploited the fact that the coefficients D_0 and D_1 in Eq. (4) are actually not independent. The weakly fluctuating scaling density ϕ_2 is the critical part of the entropy per unit volume, so that in the two-phase region at average overall density $\rho=\rho_c$,

$$\phi_2 \simeq \Delta\hat{S} = \int \frac{(\hat{C}_V)_{\rm cr}}{T} dT$$
$$\simeq -\frac{A_0^-}{1-\alpha}|\Delta\hat{T}|^{1-\alpha}\left(1 + \frac{1-\alpha}{1-\alpha+\theta}A_1^-|\Delta\hat{T}|^{\theta}\right) + \hat{B}_{\rm cr}|\Delta\hat{T}|, \quad (43)$$

where

$$(\hat{C}_V)_{\rm cr} \simeq A_0^-|\Delta\hat{T}|^{-\alpha}(1 + A_1^-|\Delta\hat{T}|^{\theta}) - \hat{B}_{\rm cr} \quad (44)$$

is the critical (fluctuation-induced) part of the isochoric heat capacity in the two-phase region and $B_{\rm cr}$ the so-called "critical background;" $\hat{B}_{\rm cr}=B_{\rm cr}/k_B$ is also a fluctuation-induced, but analytical, part of the heat capacity. The correction-to-asymptotic-scaling amplitude in the two-phase region A_1^- is approximately equal to the corresponding correction amplitude A_1^+ above the critical temperature [48], while $A_0^+/A_0^- \simeq 0.523$ [18]. Therefore, Eq. (31) can be reexpressed as

$$\hat{\rho}_d - 1 \simeq \frac{a_3}{1+a_3}B_0^2|\Delta\hat{T}|^{2\beta} - b_2\left(\frac{A_0^-}{(1-\alpha)}|\Delta\hat{T}|^{1-\alpha} - \hat{B}_{\rm cr}|\Delta\hat{T}|\right). \quad (45)$$

Since $D_0=b_2\hat{B}_{\rm cr}$, Eqs. (31) and (45) contains only two adjustable parameters, a_3 and b_2.

The critical background was studied by Bagnuls and Bervillier in a three-dimensional field theory [48] and by Anisimov *et al.* in crossover theory based on a renormalized Landau expansion [49]. According to the theory

$$\hat{B}_{\rm cr} = \frac{A_0^+(A_1^+)^{\alpha/\theta}}{R_0(1-\bar{u})^{\alpha/\theta}}, \quad (46)$$

where $R_0 \simeq 0.7$ is a universal number [48,49]; the parameter $\bar{u}$ is an effective coupling constant which depends on the cutoff wave number Λ of the critical fluctuations. In the infinite-cutoff limit $\bar{u}$ is zero and relation (46) becomes universal [48,49]. For the lattice-gas (Ising) model $\Lambda=1$ [38] and of order unity for simple molecular fluids [49]. Furthermore, for many simple fluids $\bar{u}\simeq 0.4-0.5$ [49]. Since the exponent $\alpha/\theta \simeq 0.2$ is small and $\bar{u}$ does not change much, the relation between $\hat{B}_{\rm cr}$, A_0^+, and A_1^+ for many simple fluids is almost universal. Furthermore, since for $\bar{u}\simeq 0.4-0.5$ the correction amplitude $A_1^+ \lesssim 1$, it is expected $\hat{B}_{\rm cr} \lesssim A_0^+$. Unfortunately, only for a few fluids, such as methane [50] and ethane [51], the available heat-capacity data in the two-phase region are accurate enough to estimate $\hat{B}_{\rm cr}$ with Eq. (46). Accurate heat-capacity data for SF_6 have been obtained in a microgravity experiment by Haupt and Straub [52]. Barmatz *et al.* [53] fitted these data to crossover theory and obtained an insignificant value of $A_1^{\pm}$. This result, while it seems a bit surprising, means that the value of $\bar{u}$ for SF_6 may be close to unity. In this case Eq. (46) cannot be used. However, Eq. (46) can be modified to a form that does not contain $\bar{u}$ and the amplitude A_1^+. By using expressions for A_0^+ and A_1^+ from the crossover theory [49,54], one can obtain an explicit equation for $B_{\rm cr}$,

$$\hat{B}_{\rm cr} = \frac{a_0^2}{\alpha u_0}\nu u^*, \quad (47)$$

where the constant u^* is a coupling constant in the renormalization group theory. For the three-dimensional Ising universality class $u^* \simeq 0.47$ [49]. Equation (47) contains the system-dependent ratio $a_0^2/u_0=(1/3)\bar{\Delta}\hat{C}_V$, where $\bar{\Delta}\hat{C}_V$ is the mean-field heat-capacity discontinuity at the critical point. The asymptotic scaling amplitude A_0^+ is also proportional to the ratio a_0^2/u_0, while B_0 is proportional to $(a_0/u_0)^{1/2}$ [54]. For the van der Waals fluid $\bar{\Delta}\hat{C}_V=9/2$ so that, with $a_0^2/u_0 =3/2$ and $\nu u^*/\alpha \simeq 2.7$, the critical background $\hat{B}_{\rm cr}\simeq 4$, corresponding to $B_{\rm cr}\simeq 33$ J/mol K.

Another way to estimate $B_{\rm cr}$ is to subtract the "ideal-gas" heat capacity from the total heat-capacity background in the one-phase region. This method may give realistic values of $B_{\rm cr}$ for some simple fluids. The ideal-gas heat capacity for simple fluids can be found in the literature (e.g., Ref. [55]). For SF_6, methane, and nitrogen this procedure gives the critical background 32 J/mol K, 30 J/mol K, and 29 J/mol K, correspondingly. These values are very close to that obtained for the van der Waals fluid and (for methane) also to the value obtained with Eq. (46). However, for ethane we obtained a larger value, 57 J/mol K, which correlates with a larger leading critical amplitudes A_0^- and B_0, presented in Table I, and close to $B_{\rm cr}\simeq 50$ J/mol K obtained with Eq. (46). Similar values of $B_{\rm cr}$ are obtained for the simulated hard-core square-well (HCSW) model and the restricted primitive model (RPM). The amplitudes A_0^+ for HCSW and RPM were reliably calculated with the three-scale factor of universality $\alpha\Gamma_0^+A_0^+/B_0^2 \simeq 0.0581$ [18], where the amplitudes Γ_0^+ and B_0 were taken from Refs. [56,57]. The values of $A_0^- \simeq A_0^+/0.523$ were fixed in fits of the simulated heat-capacity data for HCSW [57] and RPM [58] to obtain $B_{\rm cr}$.

Although the critical background is a difficult parameter to obtain accurately, we conclude that (with a possible exception for SF_6) $\hat{B}_{\rm cr}$ is of the same order of magnitude as the leading amplitude $A_0^+ \simeq 0.5A_0^-$; indeed, for several fluids $\hat{B}_{\rm cr} \simeq (0.4-0.5)A_0^-$. A relatively large value, 150 J/mol K obtained for *n*-heptane could be possibly an overestimate, which might be caused by an error in the evaluation of the heat-capacity regular background through the ideal-gas heat capacity.

We have examined a number of systems, including several hydrocarbons, as well as two simulated models, namely the HCSW model and the RPM of electrolyte. The HCSW fluids consist of hard spheres with the diameter d, the attractive square well of depth ϵ and interaction range $1.5d$ [56]. The RPM consists of an equal number of positive and negative ions with hard-core diameter d [56]. The ions have charges $\pm q_0$ and interact with each other via the Coulombic potential. The potential energy $\varphi(r)=\pm q_0^2/\varepsilon r$, where r is the interparticle distance and ε is the dielectric constant of medium. The critical densities for HCSW and RPM listed in Table I are made dimensionless as $\rho_c d^3$ for both models, while the critical temperatures are k_BT_c/ϵ (HCSW) and $k_BT_c\varepsilon d/q_0^2$ (RPM).

TABLE I. Critical parameters, amplitudes, normalized critical density, and asymmetry parameters for the studied systems. Notes: * indicates reduced critical parameters. The values in parentheses are obtained by interpolation.

	T_c (K)	ρ_c (mol/diam^3)	A_0^- (J/mol K)	$B_{\rm cr}$ (J/mol K)	B_0	ρ_0^*	a_3	b_2	$10^3\sigma$
HD cxc [14]	35.957	16.07	(65)	–30	1.358	0.3469	–0.0127	–0.0593	0.03
Neon cxc [14]	44.479	23.97	(70)	–30	1.497	0.3221	–0.0177	–0.0683	0.03
Methane cxc [65], C_V [50]	190.551	10.14	75	–30	1.551	0.3025	–0.0238	–0.0730	0.08
Nitrogen cxc [14], C_V [59]	126.214	11.20	78	–29	1.565	0.2884	–0.0177	–0.0701	0.04
Ethene cxc [14]	282.377	7.665	(90)	–50	1.642	0.2506	–0.0035	–0.0745	0.28
Ethane cxc [14], C_V [51]	305.363	6.851	98	–57	1.649	0.2293	0.0014	–0.0603	0.41
HCSW cxc [56], C_V [57]	1.218*	0.3076*	69	–51	1.926	0.3140	0.0083	–0.0529	0.77
RPM cxc [56], C_V [58]	0.0507*	0.0760*	97	–41	3.635	0.1479	0.137	–0.483	0.51
Water cxc [69], C_V [70]	647.096	17.84	116	(–47)	2.035	0.1861	0.0618	–0.0482	0.45
n-pentane cxc [66,67], C_V [71]	469.610	3.204	157	(–63)	1.776	0.1436	0.110	0.0207	1.00
SF$_6$ cxc [11], C_V [52,53]	318.707	5.012	143	–32	1.733	0.1576	0.181	0.0351	0.40
Freon-113 cxc [12]	486.968	3.026	(165)	(–66)	1.841	0.1367	0.218	0.0483	0.53
n-heptane cxc [68], C_V [71]	539.860	2.318	188	–150	1.843	0.1201	0.369	0.0941	1.60

For some of the systems presented in Table I we could find both heat-capacity and coexistence data in the near-asymptotic range $10^{-4}<|\Delta\hat{T}|<0.01$. In this range the terms of higher order than linear in Eq. (45) are within experimental errors. Experimental data closer than $|\Delta\hat{T}|<10^{-4}$ were avoided as they might be affected by errors in ρ_c and T_c and by other factors, such as gravity, impurities, etc. [3]. We fitted the difference in the densities, $\rho'-\rho''$, of the experimental coexistence data to $(\rho'-\rho'')/2\rho_c=B_0|\Delta\hat{T}|^{\beta}$ to obtain B_0 and the available heat-capacity data to Eq. (44) to obtain A_0^- and A_1^- (when it was possible). For several simple fluids there are accurate vapor-liquid coexistence data, but no reliable heat-capacity data in the critical region. However, since A_0^- is a smooth function of the critical parameters within a group of substances obeying the law of corresponding states, the values of A_0^- for HD, neon, ethene, and Freon-113 can be reliably obtained by interpolation. The critical background for neon and HD was fixed at the methane value $B_{\rm cr}=30$ J/(mol K) and for ethene at the value $B_{\rm cr}=50$ J/(mol K). Since the parameter $B_{\rm cr}$ may be estimated with a significant error (in some cases up to 20–30 %), we have also investigated the effect of such an error on the values of the asymmetry parameters a_3 and b_2. The effect on complete-scaling coefficient a_3 is less significant than that on b_2, which is in turn smaller than the error in $B_{\rm cr}$. (See Fig. 3.)

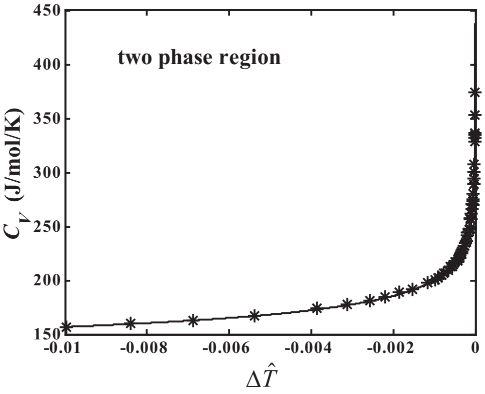

FIG. 3. Heat-capacity data for ethane in the two-phase region [59]. The solid line is a fit to Eq. (44).

The means of the liquid and vapor densities, $(\rho'+\rho'')/2\rho_c$, were fitted to Eq. (45) to obtain a_3 and b_2. The results of the fits, including the standard deviations σ, are presented in Table I and illustrated by Figs. 4–15. In addition, in Table I we present the values of normalized "interaction volumes" ρ_0^*, defined as $\rho_0^*=8\xi_0^3\rho_c$, where ξ_0^+, the amplitude of the correlation length in the one-phase region, represents the range of intermolecular interactions. This amplitude can be directly obtained from a light-scattering experiment [3] or from the heat-capacity amplitude A_0^+ through two-scale factor of universality, $A_0^+\rho_c\xi_0^3\simeq 0.171$ [2,18], such that $\rho_0^*\simeq 1.37/A_0^+\simeq 2.62/A_0^-$. The parameter $\rho_0^*=\rho_c(8\xi_0^3)$ can be also interpreted as the reduced critical density (normalized by the "density of interactions").

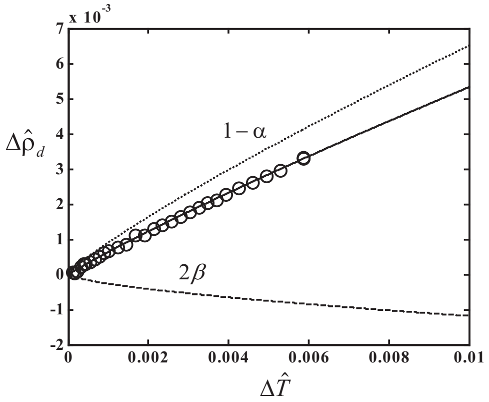

FIG. 4. The liquid-vapor diameter for HD. The circles indicate experimental data [14]. Curves, solid line is a fit to Eq. (45), dashed line represents the 2β term, and dotted line represents both $1-\alpha$ and linear terms.

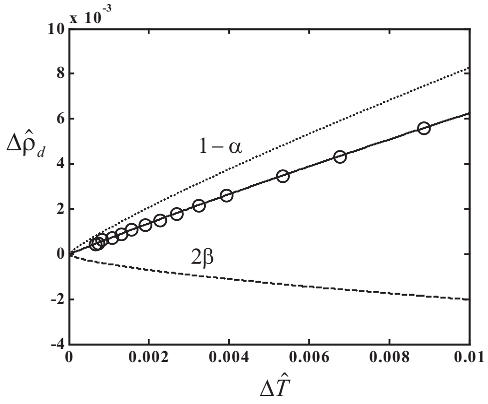

FIG. 5. The liquid-vapor diameter for neon. The circles indicate experimental data [14]. Curves, solid line is a fit to Eq. (45), dashed line represents the 2β term, and dotted line represents both $1-\alpha$ and linear terms.

The fluids presented in Table I may be divided in two groups, from HD to ethane and from water to *n*-heptane. For the first group, the parameter a_3 is very small (either negative or positive) while the parameter b_2 is negative. In such fluids the "diameters" are mostly controlled by the terms proportional to $|\Delta\hat{T}|^{1-\alpha}$ and $|\Delta\hat{T}|$. Moreover, when both $a_3 > 0$ and $b_2 < 0$, the two non-analytic contributions may largely compensate each other, producing an imitation of a rectilinear diameter (from HD to nitrogen, as seen in Figs. 4–7). Such compensation can explain why the "diameters" observed in some simple fluids seem almost rectilinear [8,9]. For the second group, a_3 relatively large and positive while b_2 is small and usually positive. For such fluids the "diameters" are very much curved; they are mostly controlled by the term $\propto|\Delta\hat{T}|^{2\beta}$ originating from "complete scaling" (see Figs. 12–15). One can also notice that the fluids in the first group have relatively large critical molar densities and small molecular volumes or, in terms of ρ_0^*, large interaction volume with respect to the molecular volume. The fluids in the second group have relatively small critical molar densities and large molecular volumes (small interaction volumes with respect to the molecular volumes).

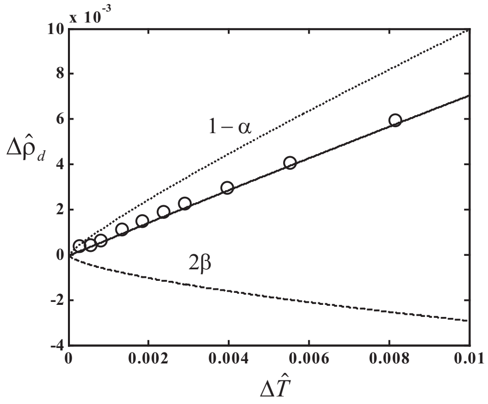

FIG. 6. The liquid-vapor diameter for methane. The circles indicate experimental data [65]. Curves, solid line is a fit to Eq. (45), dashed line represents the 2β term, and dotted line represents both $1-\alpha$ and linear terms.

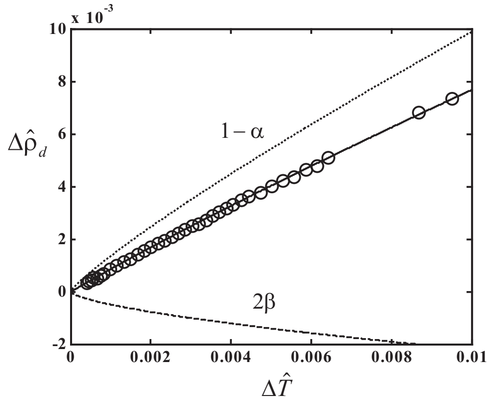

FIG. 7. The liquid-vapor diameter for nitrogen. The circles indicate experimental data [14]. Curves, solid line is a fit to Eq. (45), dashed line represents the 2β term, and dotted line represents both $1-\alpha$ and linear terms.

Two simulated models, HCSW and RPM, are somewhere between these two groups. As seen from Figs. 10 and 11, the "diameter" in these models is controlled by both $\propto|\Delta\hat{T}|^{2\beta}$ and $\propto|\Delta\hat{T}|^{1-\alpha}+\alpha|\Delta\hat{T}|$ contributions. The diameter in RPM looks very much similar to that in water (Fig. 12) with almost equal contributions from both sources of asymmetry.

VI. FLUID ASYMMETRY IN MEAN-FIELD APPROXIMATION

The asymmetry coefficients a_3 and b_2 are system-dependent; they are determined by details of intermolecular interactions. This is why it is reasonable to assume that fluctuations do not significantly affect the values of these parameters. In other words, we assume that, while the physical properties are strongly affected by fluctuations in the critical region, the relations between the theoretical scaling fields and the physical fields are not. This assumption opens the way for predicting the values of a_3 and b_2 from mean-field equations of state.

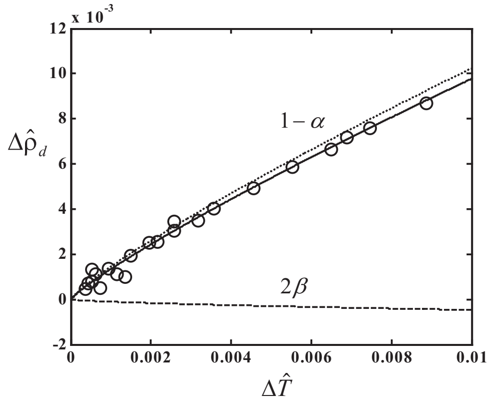

FIG. 8. The liquid-vapor diameter for ethene. The circles indicate experimental data [14]. Curves, solid line is a fit to Eq. (45), dashed line represents the 2β term, and dotted line represents both $1-\alpha$ and linear terms.

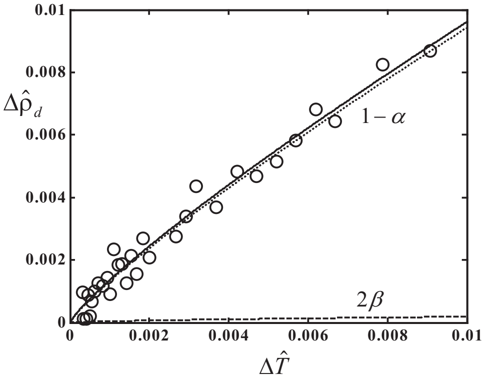

FIG. 9. The liquid-vapor diameter for ethane. The circles indicate experimental data [14]. Curves, solid line is a fit to Eq. (45), dashed line represents the 2β term, and dotted line represents both $1-\alpha$ and linear terms.

In mean-field approximation the field-dependent potential $-h_3$ is given by Eq. (13). The critical part of the order-parameter-dependent thermodynamic potential ψ is obtained through a Legendre transformation as

$$\psi = -h_3 + h_1\phi_1 = \tfrac{1}{2}a_0 h_2 \phi_1^2 + \tfrac{1}{24}u_0\phi_1^4. \tag{48}$$

The ordering field is obtained as

$$h_1 = \frac{\partial\psi}{\partial\phi_1} = a_0 h_2 \phi_1 + \tfrac{1}{6}u_0\phi_1^3. \tag{49}$$

In zero field ($h_1=0$) below the critical temperature Eq. (49) yields the symmetric order parameter

$$\phi_1 = \pm\left(\frac{6a_0}{u_0}\right)^{1/2}(-h_2)^{1/2} \tag{50}$$

while

$$\phi_2 = \frac{3a_0^2}{u_0}h_2. \tag{51}$$

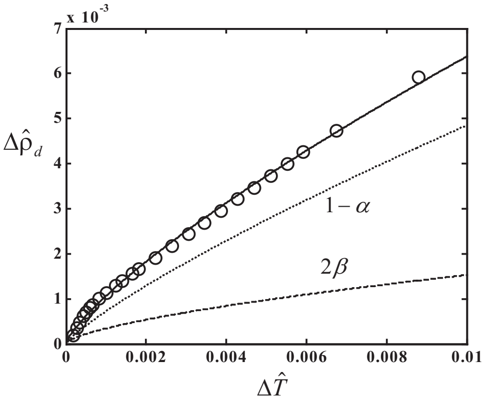

FIG. 10. The liquid-vapor diameter for HCSW. The circles indicate experimental data [56]. Curves, solid line is a fit to Eq. (45), dashed line represents the 2β term, and dotted line represents both $1-\alpha$ and linear terms.

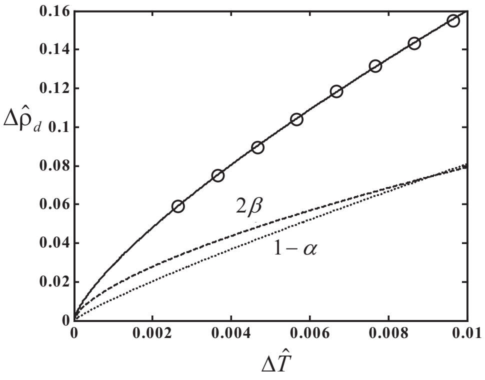

FIG. 11. The liquid-vapor diameter for RPM. The circles indicate experimental data [56]. Curves, solid line is a fit to Eq. (45), dashed line represents the 2β term, and dotted line represents both $1-\alpha$ and linear terms.

The actual asymmetric behavior of the vapor and liquid densities is revealed by specific relations between the scaling fields and the physical fields.

A. "Incomplete scaling" in mean-field approximation

With the convenient choice of the critical entropy value, $\hat{S}_c=(d\hat{P}/d\hat{T})_{\mathrm{cxc},c}$ and with neglect of the pressure mixing in the ordering field h_1 [$a_3=0$ in Eq. (26)] the scaling fields and densities read

$$h_1 = \Delta\hat{\mu}, \quad h_2 = \Delta\hat{T} + b_2\Delta\hat{\mu}, \tag{52}$$

$$\phi_1 = \Delta\hat{\rho} - b_2\Delta(\hat{\rho}\hat{S}), \quad \phi_2 = \Delta(\hat{\rho}\hat{S}). \tag{53}$$

Expanding the chemical potential as

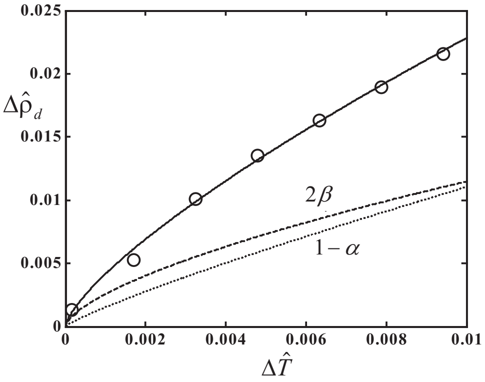

FIG. 12. The liquid-vapor diameter for water. The circles indicate experimental data [69]. Curves, solid line is a fit to Eq. (45), dashed line represents the 2β term, and dotted line represents both $1-\alpha$ and linear terms.

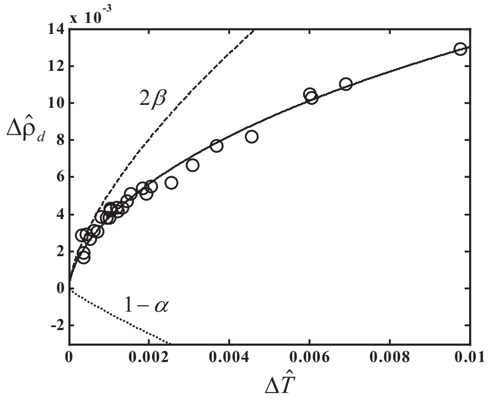

FIG. 13. The liquid-vapor diameter for SF_6. The circles indicate experimental data [11]. Curves, solid line is a fit to Eq. (45), dashed line represents the 2β term, and dotted line represents both $1-\alpha$ and linear terms.

$$\Delta\hat{\mu} = \hat{\mu}_{11}\Delta\hat{\rho}\Delta\hat{T} + \tfrac{1}{6}\hat{\mu}_{30}\Delta\hat{\rho}^3 + \tfrac{1}{2}\hat{\mu}_{21}\Delta\hat{\rho}^2\Delta\hat{T} + \tfrac{1}{24}\hat{\mu}_{40}\Delta\hat{\rho}^4 + \cdots \tag{54}$$

and finding in first approximation $\Delta(\hat{\rho}\hat{S}) = -(1/2)\hat{\mu}_{11}\Delta\hat{\rho}^2$, we obtain from Eqs. (49), (52), and (53),

$$h_1 = \Delta\hat{\mu} = \hat{\mu}_{11}\Delta\hat{\rho}\Delta\hat{T} + \tfrac{1}{6}\hat{\mu}_{30}\Delta\hat{\rho}^3 + \tfrac{3}{2}\hat{\mu}_{11}b_2\Delta\hat{\rho}^2\Delta\hat{T} + \tfrac{5}{12}\hat{\mu}_{30}b_2\Delta\hat{\rho}^4 + \cdots, \tag{55}$$

where $\hat{\mu}_{ij} = \partial^{i+j}\hat{\mu}/\partial\Delta\hat{\rho}^i\partial\Delta\hat{T}^j$ are the derivatives of the chemical potential taken at the critical point.

Comparing Eqs. (55) and (54) we obtain $a_0 = \hat{\mu}_{11}$, $u_0 = \hat{\mu}_{30}$, $\hat{\mu}_{21} = 3\hat{\mu}_{11}b_2$, $\hat{\mu}_{40} = 10\hat{\mu}_{30}b_2$, and the relation between $\hat{\mu}_{21}$ and $\hat{\mu}_{40}$,

$$\frac{2\hat{\mu}_{21}}{\hat{\mu}_{11}} = \frac{3\hat{\mu}_{40}}{5\hat{\mu}_{30}}. \tag{56}$$

Therefore, in "incomplete scaling" only one mixing coefficient, b_2, is responsible for fluid asymmetry in the critical region.

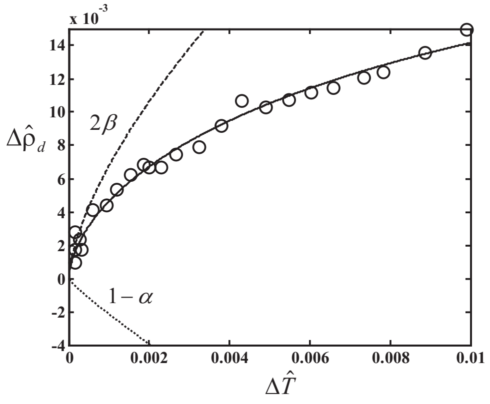

FIG. 14. The liquid-vapor diameter for Freon-113. The circles indicate experimental data [64]. Curves, solid line is a fit to Eq. (45), dashed line represents the 2β term, and dotted line represents both $1-\alpha$ and linear terms.

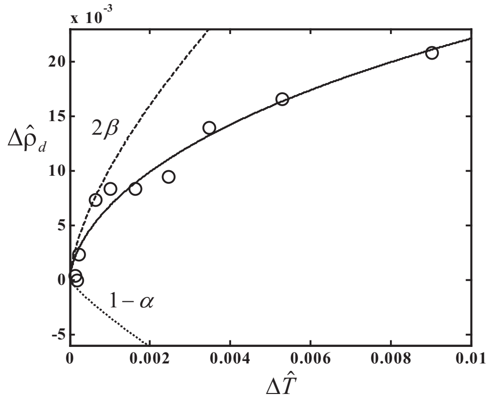

FIG. 15. The liquid-vapor diameter for *n*-heptane. The circles indicate experimental data [12]. Curves, solid line is a fit to Eq. (45), dashed line represents the 2β term, dotted line represents both $1-\alpha$ and linear terms.

However, for the simplest equation of state that describes real-fluid behavior, the van der Waals equation, the term $(1/2)\hat{\mu}_{21}\Delta\hat{\rho}^2\Delta\hat{T}$ is absent, while the term $(1/24)\hat{\mu}_{40}\Delta\hat{\rho}^4$ exists. This cannot happen if the both terms are proportional to the same asymmetry coefficient b_2. The existence of the independent asymmetry term makes exact mapping of fluids into the lattice-gas model by "incomplete scaling" impossible. Moreover, in "incomplete scaling" there is no discontinuity in the second derivative $d\hat{\mu}^2/d\hat{T}^2$ along the phase coexistence and $(\partial^2\hat{\mu}/\partial\hat{T}^2)_\rho$ along the critical isochore above the critical temperature. Indeed, since for this discontinuity thermodynamics yields [2]

$$\left(\frac{d^2\hat{\mu}}{d\hat{T}^2}\right)_{\text{cxc}} - \left(\frac{\partial^2\hat{\mu}}{\partial\hat{T}^2}\right)_{\rho=\rho_c} = -\frac{\hat{\mu}_{11}^2}{\hat{\mu}_{30}}\left(\frac{2\hat{\mu}_{21}}{\hat{\mu}_{11}} - \frac{3\hat{\mu}_{40}}{5\hat{\mu}_{30}}\right), \tag{57}$$

it is straightforward from Eq. (56) that the discontinuity disappears in the traditional "incomplete scaling."

B. "Complete scaling" in mean-field approximation

In "complete scaling," given by Eqs. (26)–(28), in order to obtain the expressions of a_3 and b_2 in terms of $\hat{\mu}_{ij}$, one needs to expand both $\Delta\hat{\mu}$ and $\Delta\hat{P}$,

$$\Delta\hat{\mu} = \hat{\mu}_{01}\Delta\hat{T} + \hat{\mu}_{02}\Delta\hat{T}^2 + \hat{\mu}_{11}\Delta\hat{\rho}\Delta\hat{T} + \tfrac{1}{6}\hat{\mu}_{30}\Delta\hat{\rho}^3 + \tfrac{1}{2}\hat{\mu}_{21}\Delta\hat{\rho}^2\Delta\hat{T} + \tfrac{1}{24}\hat{\mu}_{40}\Delta\hat{\rho}^4 + \cdots, \tag{58}$$

$$\Delta\hat{P} = \hat{P}_{01}\Delta\hat{T} + \hat{P}_{02}\Delta\hat{T}^2 + \hat{P}_{11}\Delta\hat{\rho}\Delta\hat{T} + \tfrac{1}{6}\hat{P}_{30}\Delta\hat{\rho}^3 + \tfrac{1}{2}\hat{P}_{21}\Delta\hat{\rho}^2\Delta\hat{T} + \tfrac{1}{24}\hat{P}_{40}\Delta\hat{\rho}^4 + \cdots, \tag{59}$$

where the derivatives $\hat{P}_{ij} = \partial^{i+j}\hat{P}/\partial\hat{\rho}^i\partial\hat{T}^j$ are taken at the critical point. Since $\hat{\mu}_{01} = (\partial\hat{\mu}/\partial\hat{T})_{h_1=0,c} = 0$ [by adopting $\hat{S}_c = (d\hat{P}/d\hat{T})_{\text{cxc},c}$] and $a_2 + a_3\hat{P}_{01} = a_2 + a_3(\partial\hat{P}/\partial\hat{T})_{h_1=0,c} = 0$, the expansion of h_1, given by Eq. (49), becomes

$$h_1 = (\hat{\mu}_{11} + a_3\hat{P}_{11})\Delta\hat{\rho}\Delta\hat{T} + \tfrac{1}{6}(\mu_{30} + a_3\hat{P}_{30})\Delta\hat{\rho}^3 + \tfrac{1}{2}(\hat{\mu}_{21} + a_3\hat{P}_{21})\Delta\hat{\rho}^2\Delta\hat{T} + \tfrac{1}{24}(\hat{\mu}_{40} + a_3\hat{P}_{40})\Delta\hat{\rho}^4 + \cdots . \tag{60}$$

Thermodynamic relations between μ_{ij} and P_{ij}, such as $\hat{P}_{11} = \hat{\mu}_{11}$, $\hat{P}_{30} = \hat{\mu}_{30}$, $\hat{P}_{21} = \hat{\mu}_{21} + \hat{\mu}_{11}$, and $\hat{P}_{40} = \hat{\mu}_{40} + 3\hat{\mu}_{30}$ [2], help to simplify Eq. (60) as

$$h_1 = (1 + a_3)\hat{\mu}_{11}\Delta\hat{\rho}\Delta\hat{T} + \tfrac{1}{6}(1 + a_3)\hat{\mu}_{30}\Delta\hat{\rho}^3 + \tfrac{1}{2}[(1 + a_3)\hat{\mu}_{21} + a_3\hat{\mu}_{11}]\Delta\hat{\rho}^2\Delta\hat{T} + \tfrac{1}{24}[(1 + a_3)\hat{\mu}_{40} + 3a_3\hat{\mu}_{30}]\Delta\hat{\rho}^4 + \cdots . \tag{61}$$

By using $\phi_2 \approx -(1/2)a_0\phi_1^2$, and $\phi_1 \approx [1/(1+a_3)]\Delta\hat{\rho} - [1/2(1+a_3)]\Delta\hat{\rho}^2 + [a_3/(1+a_3)^2]\mu_{11}b_2\Delta\hat{\rho}^2$, we reexpress expansion (49) in terms of $\Delta\hat{\rho}$ and $\Delta\hat{T}$,

$$\begin{aligned} h_1 &= a_0 h_2 \phi_1 + \frac{1}{6}u_0\phi_1^3 \\ &= \frac{a_0}{1 + a_3}\Delta\hat{\rho}\Delta\hat{T} + \frac{1}{6}u_0\frac{1}{(1 + a_3)^3}\Delta\hat{\rho}^3 \\ &\quad + \left(\frac{\hat{\mu}_{11}^2 b_2}{1 + a_3} - \frac{\hat{\mu}_{11}a_3}{(1 + a_3)^2} + \frac{\hat{\mu}_{11}^2}{2(1 + a_3)}b_2\right)\Delta\hat{\rho}^2\Delta\hat{T} \\ &\quad + \left(\frac{\hat{\mu}_{11}\hat{\mu}_{30}b_2}{6(1 + a_3)} + \frac{-a_3u_0}{2(1 + a_3)^4} + \frac{\hat{\mu}_{11}u_0b_2}{4(1 + a_3)^3}\right)\Delta\hat{\rho}^4 + \cdots . \end{aligned} \tag{62}$$

The coefficients of each corresponding term in Eqs. (61) and (62) must be equal. This condition yields four equations with four unknown parameters a_0, u_0, a_3, and b_2. It is straightforward that terms $\propto\Delta\hat{\rho}\Delta\hat{T}$ and $\propto\Delta\hat{\rho}^3$ yield the relations $a_0 = (1+a_3)^2\mu_{11}$ and $u_0 = (1+a_3)^4\mu_{30}$, which make the mean-field amplitude for the symmetric order parameter expressed as

$$\hat{B}_0 = \left(\frac{6a_0}{u_0}\right)^{1/2} = \frac{1}{1 + a_3}\bar{B}_0 = \frac{1}{1 + a_3}\left(\frac{6\hat{\mu}_{11}}{\hat{\mu}_{30}}\right)^{1/2}. \tag{63}$$

The amplitude $\hat{B}_0$ differs from the mean-field amplitude $\bar{B}_0$ for the coexisting densities by the same prefactor $(1+a_3)^{-1}$ as in the relation between the Ising amplitude for the order parameter and the scaling amplitude B_0 given by Eq. (32). The comparison of each asymmetry term, $\propto\Delta\hat{\rho}^2\Delta\hat{T}$ or $\propto\Delta\hat{\rho}^4$ in Eq. (61) and Eq. (62), results in two equations involving only two unknowns, a_3 and b_2. The slope of the rectilinear linear diameter [2]

$$D = \frac{\hat{\mu}_{21}}{\hat{\mu}_{30}} - \frac{3\hat{\mu}_{11}\hat{\mu}_{40}}{5\hat{\mu}_{30}^2}. \tag{64}$$

The condition $h_1 = 0$ for the coexistence curve can be solved by iteration to obtain the slope of the rectilinear diameter. From Eq. (61), which contains only a_3, at $h_1 = 0$ we obtain

$$a_3 = \left(\frac{2}{3}\frac{\hat{\mu}_{21}}{\hat{\mu}_{11}} - \frac{\hat{\mu}_{40}}{5\hat{\mu}_{30}}\right) \bigg/ \left(1 - \frac{2}{3}\frac{\hat{\mu}_{21}}{\hat{\mu}_{11}} + \frac{\hat{\mu}_{40}}{5\hat{\mu}_{30}}\right). \tag{65}$$

By rearranging this expression we have a simple equation to be used in the further analyses,

$$\frac{a_3}{1 + a_3} = \frac{2}{3}\frac{\hat{\mu}_{21}}{\hat{\mu}_{11}} - \frac{1}{5}\frac{\hat{\mu}_{40}}{\hat{\mu}_{30}}. \tag{66}$$

By applying the condition $h_1 = 0$ to Eq. (62) and using Eq. (66) we obtain the expression of b_2 in terms of $\hat{\mu}_{ij}$,

$$b_2 = \frac{1}{\hat{\mu}_{11}}\left(\frac{\hat{\mu}_{21}}{\hat{\mu}_{11}} - \frac{1}{5}\frac{\hat{\mu}_{40}}{\hat{\mu}_{30}}\right). \tag{67}$$

By separating the slope of the rectilinear diameter given by Eq. (64) into two parts, a_3 contribution and b_2 contribution, one obtains

$$D = \frac{a_3}{1 + a_3}\frac{6\hat{\mu}_{11}}{\hat{\mu}_{30}} - b_2\frac{3\mu_{11}^2}{\hat{\mu}_{30}}. \tag{68}$$

The result is equivalent to the slope obtained from Eq. (31) in mean-field approximation by substituting $\phi_1^2 = (6a_0/u_0) \times (-\Delta\hat{T})$, $\phi_2 = (3a_0^2/u_0)\Delta\hat{T}$, $a_0 = (1+a_3)^2\hat{\mu}_{11}$, and $u_0 = (1+a_3)^4\hat{\mu}_{30}$. One may notice that $6\hat{\mu}_{11}/\hat{\mu}_{30}$ is the square of the mean-field amplitude $\bar{B}_0$ while $3\hat{\mu}_{11}^2/\hat{\mu}_{30}$ is the mean-field heat-capacity discontinuity $\bar{\Delta}\hat{C}_V$ at the critical point. Finally,

$$D = \frac{a_3}{1 + a_3}B_0^2 - b_2\bar{\Delta}\hat{C}_V. \tag{69}$$

Since in mean-field approximation $\alpha = 0$ and $\beta = 0.5$, both terms, $\propto|\Delta\hat{T}|^{2\beta}$ and $\propto|\Delta\hat{T}|^{1-\alpha}$, in Eq. (31) become linear. Furthermore, the relation between the isochoric heat-capacity discontinuity $\bar{\Delta}\hat{C}_V$ at the critical density and the mean-field discontinuity of the chemical potential $\bar{\Delta}\hat{\mu}$ reads

$$\frac{a_3}{1 + a_3}\bar{\Delta}\hat{C}_V = -\bar{\Delta}\hat{\mu} = \frac{\hat{\mu}_{11}^2}{\hat{\mu}_{30}}\left(\frac{2\hat{\mu}_{21}}{\hat{\mu}_{11}} - \frac{3\hat{\mu}_{40}}{5\hat{\mu}_{30}}\right) \tag{70}$$

which is the mean-field equivalent of the complete-scaling result given by Eq. (34).

VII. ASYMMETRY COEFFICIENTS FROM MEAN-FIELD EQUATIONS OF STATE

Expressions (66) and (67) can be used to obtain the values of the asymmetry coefficients a_3 and b_2 from mean-field ("classical") equations of state. All analytic mean-field equations of state asymptotically yield a quadratic parabola and a rectilinear diameter for the coexistence curve, and a finite discontinuity in the isochoric heat capacity at the critical density [60] as explained in Sec. VI.

A. van der Waals model

The van der Waals equation in (P,ρ,T) variables reads

$$P = \frac{\rho k_B T}{1 - b\rho} - a\rho^2, \qquad (71)$$

where a and b are system-dependent constants associated with attraction and repulsion between molecules, respectively. By rescaling $\tilde{\rho}=b\rho, \tilde{P}=Pb$, and $\tilde{a}=a/b$, we obtain

$$\frac{\tilde{P}}{k_B T} = \frac{\tilde{\rho}}{1 - \tilde{\rho}} - \frac{\tilde{a}\tilde{\rho}^2}{k_B T}. \qquad (72)$$

The coordinates of the critical point can be found from the stability conditions

$$\left(\frac{\partial \mu}{\partial \rho}\right)_T = \frac{1}{\rho}\left(\frac{\partial P}{\partial \rho}\right)_T = 0, \qquad (73)$$

$$\left(\frac{\partial^2 \mu}{\partial \rho^2}\right)_T = -\frac{1}{\rho^2}\left(\frac{\partial P}{\partial \rho}\right)_T + \frac{1}{\rho}\left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0 \qquad (74)$$

as

$$\frac{k_B T_c}{\tilde{a}} = \frac{8}{27}, \quad \tilde{\rho}_c = \frac{1}{3}. \qquad (75)$$

By integration, one can obtain the density of the Helmholtz energy for the van der Waals fluid,

$$\Delta(\tilde{\rho}\hat{A}) = \frac{\tilde{\rho}A - \tilde{\rho}A_{\mathrm{ig}}}{k_B T} = \tilde{\rho}\ln\frac{\tilde{\rho}\hat{T}}{1-\tilde{\rho}} - \tilde{\rho} - \frac{\tilde{a}\tilde{\rho}^2}{k_B T}, \qquad (76)$$

where $A_{\mathrm{ig}}=\int C_P^{\mathrm{ig}}(T)dT - T\int C_P^{\mathrm{ig}}(T)dT/T$ is the ideal-gas caloric background. The chemical potential

$$\hat{\mu} - \hat{\mu}_{\mathrm{ig}} = \ln\frac{\tilde{\rho}\hat{T}}{1-\tilde{\rho}} + \frac{\tilde{\rho}}{1-\tilde{\rho}} - \frac{2\tilde{a}\tilde{\rho}}{k_B T}, \qquad (77)$$

where $\hat{\mu}_{\mathrm{ig}}=\hat{A}_{\mathrm{ig}}$. Taking derivatives of the chemical potential with respect to density and temperature, we obtain the values of the derivatives at the critical point,

$$\hat{\mu}_{11} = 9/4, \quad \hat{\mu}_{21} = 0, \quad \hat{\mu}_{30} = -\hat{\mu}_{40} = 27/8. \qquad (78)$$

Substituting $\hat{\mu}_{ij}$ into Eq. (64), Eq. (66), and Eq. (67), we obtain the slope D of the rectilinear diameter, as well as the asymmetry coefficients a_3 and b_2 the for the van der Waals fluid,

$$D = \frac{\hat{\mu}_{21}}{\hat{\mu}_{30}} - \frac{3\hat{\mu}_{11}\hat{\mu}_{40}}{5\hat{\mu}_{30}^2} = \frac{2}{5}, \qquad (79)$$

$$a_3 = \tfrac{1}{4}, \quad b_2 = \tfrac{4}{45}. \qquad (80)$$

B. Mean-field lattice gas

The lattice-gas is a symmetric model with the zero-slope rectilinear diameter. The mean-field equation of state for the lattice gas reads [61]

$$\frac{\tilde{P}}{k_B T} = -\ln(1-\tilde{\rho}) - \frac{\tilde{a}\tilde{\rho}^2}{k_B T}, \qquad (81)$$

where the density, the pressure, and the interaction constant are rescaled as $\tilde{\rho}=\rho l_0^3, \tilde{P}=Pl_0^3$, and $\tilde{a}=al_0^{-3}$ with l_0 being lattice spacing. The chemical potential of the lattice gas is

$$\hat{\mu} - \hat{\mu}_0 = \ln\frac{\tilde{\rho}\hat{T}}{(1-\tilde{\rho})} - \frac{2\tilde{a}\tilde{\rho}}{k_B T}. \qquad (82)$$

From the critical conditions we obtain the critical parameters

$$\frac{k_B T_c}{\tilde{a}} = \frac{1}{2}, \quad \tilde{\rho}_c = \frac{1}{2} \qquad (83)$$

and the derivatives of the chemical potential at the critical point

$$\hat{\mu}_{11} = 2, \quad \hat{\mu}_{21} = 0, \quad \hat{\mu}_{30} = 4, \quad \hat{\mu}_{40} = 0. \qquad (84)$$

Since both derivatives $\hat{\mu}_{21}$ and $\hat{\mu}_{40}$ in the lattice gas are zero, it is straightforward that $a_3=0, b_2=0$, and $D=0$.

C. Fine-lattice discretization

Moghaddam *et al.* [62] developed a fine-lattice discretization model, which represents a crossover between the symmetric lattice gas and the asymmetric continuous van der Waals fluid by introducing a discretization parameter, $\zeta = l/l_0 \geqslant 1$, where l is the diameter of the spherical molecule and l_0 is the lattice spacing,

$$\frac{\tilde{P}}{k_B T} = \zeta\ln\left(1 + \frac{\tilde{\rho}}{\zeta(1-\tilde{\rho})}\right) - \frac{\tilde{a}\tilde{\rho}^2}{k_B T}, \qquad (85)$$

when $\zeta=1$ is the lattice gas limit and $\zeta\to\infty$ approaches the van der Waals fluid. This model makes it possible to transform a symmetric fluid system to an asymmetric one by tuning the discretization parameter ζ.

The chemical potential of the fine-lattice discretization model has the form

$$\hat{\mu} - \hat{\mu}_0 = \ln\frac{\tilde{\rho}\hat{T}}{1+\tilde{\rho}(1/\zeta - 1)} + \zeta\ln\left(1 + \frac{\tilde{\rho}}{\zeta(1-\tilde{\rho})}\right) - \frac{2\tilde{a}\tilde{\rho}}{k_B T}. \qquad (86)$$

Then the critical density and temperature are both functions of the parameter ζ,

$$1 + \left(\frac{2}{\zeta} - 4\right)\tilde{\rho}_c - 3\left(\frac{1}{\zeta} - 1\right)\tilde{\rho}_c^2 = 0, \qquad (87)$$

$$\frac{k_B T_c}{\tilde{a}} = 2\tilde{\rho}_c\left(\frac{1-\zeta}{1+(1/\zeta - 1)\rho_c} + \frac{\zeta}{1-\rho_c}\right)^{-1}. \qquad (88)$$

These equations can be solved numerically. Taking the derivatives $\hat{\mu}_{ij}$ and using Eqs. (64), (66), and (67), we obtain crossover from $D=0, a_3=0$, and $b_2=0$ for the lattice gas to $D=2/5, a_3=1/4$, and $b_2=4/45$ for a continuum van der Waals fluid, as shown in Figs. 16 and 17. The fine-lattice discretization model shows that the ratio of the molecular

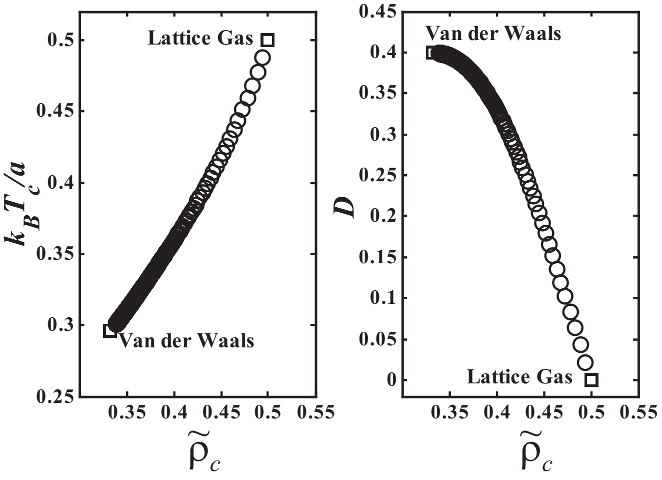

FIG. 16. Fine lattice-gas discretization model: crossover between the lattice gas and the van der Waals fluid.

size and the lattice spacing $\zeta = l/l_0$ can tune the magnitude of vapor-liquid asymmetry.

D. Effects of three-body interactions

Let c be a parameter that indicates the relative strength of three-body interactions with respect to the lattice-gas two-body interactions [14]. The chemical potential of the lattice-gas model with an extra three-body interaction term has the form

$$\hat{\mu} - \hat{\mu}_0 = \ln \frac{\tilde{\rho}\hat{T}}{1-\tilde{\rho}} - \frac{2\tilde{a}\tilde{\rho}}{k_BT}\left(1 - \frac{3}{2}c\tilde{\rho}\right). \tag{89}$$

Therefore, the critical density and temperature depend on the parameter c as

$$(6c+4)\rho_c - 9c\rho_c^2 - 2 = 0 \tag{90}$$

and

$$\frac{k_BT_c}{\tilde{a}} = \tilde{\rho}_c(1-\tilde{\rho}_c)(2-3c\tilde{\rho}_c). \tag{91}$$

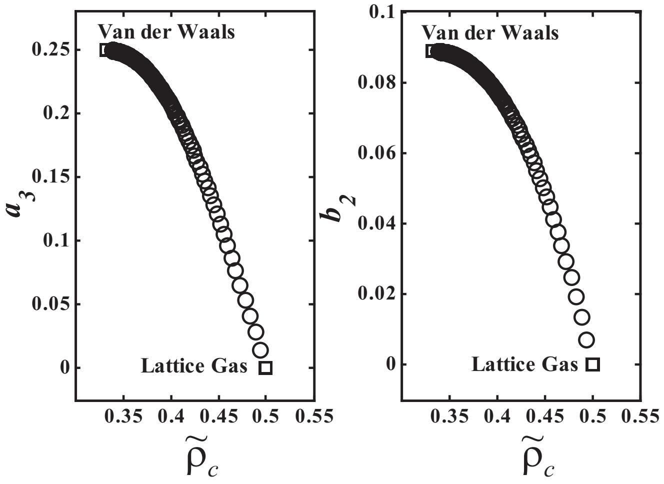

FIG. 17. Fine lattice-gas discetization model: the asymmetry coefficients versus critical densities.

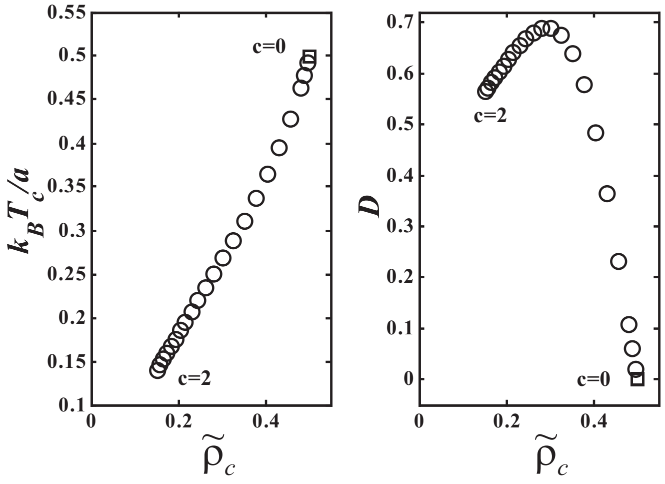

FIG. 18. Lattice-gas model with three-body interactions: crossover from symmetric lattice gas to asymmetric lattice gas.

By substituting the critical parameters into the derivatives of the chemical potential $\hat{\mu}_{ij}$ and using Eqs. (64), (66), and (67), we obtain the effects of three-body interactions on D,a_3, and b_2 for the lattice-gas model as shown in Figs. 18 and 19. The vapor-liquid asymmetry increases with increase of the contribution of three-body interactions.

E. Debye-Hückel model

An equation of state which represents the Debye-Hückel interaction between ions has the form [29]

$$\frac{\tilde{P}}{k_BT} = \frac{\tilde{\rho}}{1-\tilde{\rho}} - \frac{\tilde{a}\tilde{\rho}^{3/2}}{k_BT}. \tag{92}$$

Using the same procedure as for other mean-field equations of state we obtain $(k_BT_c)^{3/2} = 0.429\tilde{a}$, $\tilde{\rho}_c = 0.2$, $a_3 = 0.364$, and

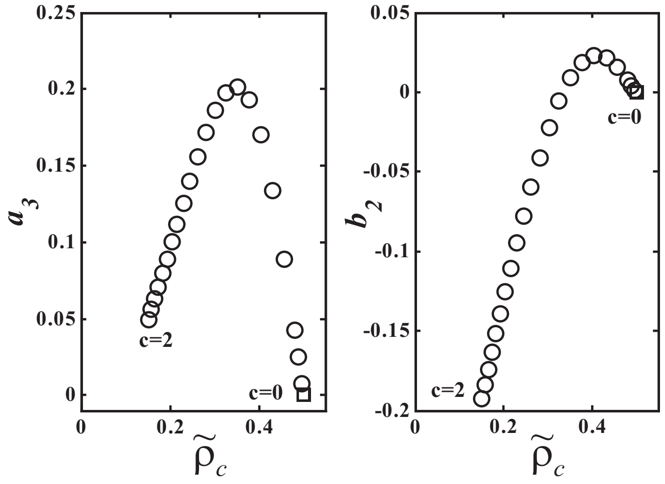

FIG. 19. Asymmetry coefficients for the lattice-gas model with three-body interactions: crossover from symmetric lattice gas to asymmetric lattice gas.

TABLE II. Dimensionless derivatives of the chemical potential and asymmetry parameters for mean-field equations of state.

	$\hat{\mu}_{11}$	$\hat{\mu}_{21}$	$\hat{\mu}_{30}$	$\hat{\mu}_{40}$	D	a_3	b_2
Lattice gas	2	0	4	0	0	0	0
van der Waals	2.25	0	3.375	−3.375	0.4	0.25	0.089
Debye-Hückel	2.344	−1.172	0.977	−2.930	3.120	0.364	0.043
Redlich-Kwong	2.739	−0.815	2.145	−5.192	1.474	0.400	0.068
Peng-Robinson							
ω=0	2.266	−0.979	1.658	−5.125	1.944	0.493	0.082
ω=0.1	2.516	−1.087	1.658	−5.125	2.158	0.493	0.074
ω=0.4	3.212	−1.388	1.658	−5.125	2.755	0.493	0.058

b_2=0.043. This result shows that the "complete scaling" contribution into the vapor-liquid asymmetry, associated with the mixing coefficient a_3, in the Debye-Hückel model is more significant than that in the van der Waals model.

F. Redlich-Kwong and Peng-Robinson equations of state

The Redlich-Kwong and Peng-Robinson equations are analytic equations commonly used in engineering [63]. In the Redlich-Kwong the van der Waals-like attraction term is made temperature dependent, such that

$$\frac{\tilde{P}}{k_BT}=\frac{\tilde{\rho}}{1-\tilde{\rho}}-\frac{\tilde{a}\tilde{\rho}^2}{k_BT^{3/2}(1+\tilde{\rho})}. \tag{93}$$

The critical parameters and asymmetry mixing coefficients for the Redlich-Kwong equation are obtained as $k_BT_c^{3/2}=0.203\tilde{a}$, $\tilde{\rho}_c$=0.26, a_3=0.4, and b_2=0.068. Therefore, the temperature dependence of the attraction part in the equation of state make the "complete scaling" vapor-liquid asymmetry, associated with the mixing coefficient a_3, more significant than that in the van der Waals model.

The Peng-Robinson equation reads

$$\frac{\tilde{P}}{k_BT}=\frac{\tilde{\rho}}{1-\tilde{\rho}}-\frac{\tilde{a}\tilde{\rho}^2\alpha}{k_BT(1+2\tilde{\rho}-\tilde{\rho}^2)}, \tag{94}$$

where $\alpha=[1+f(\omega)(1-\hat{T}^{1/2})]^2$ and $f(\omega)=(0.374\,64+1.542\,26\omega-0.269\,92\omega^2)$. In addition to a temperature dependence of the attraction term, the equation contains the so-called acentric factor ω, a phenomenological parameter associated with the shape and size of molecules. Since in the Peng-Robinson equation the acentric factor is coupled with the dependence of temperature, the fluid-phase asymmetry should strongly depend on ω. For ω=0, the critical parameters and asymmetry coefficients of the Peng-Robinson equation are obtained as $k_BT_c=0.158\tilde{a}$, ρ_c=0.221 a_3=0.493, and b_2=0.082.

The results for the classical equations of state are summarized in Table II. Interestingly, for the Peng-Robinson equation, the value of a_3 does not change as the asymmetric factor ω increases, however, since b_2 decreases, the overall asymmetry, represented by D, increases.

G. Flory-Huggins model with three-body interactions

The chemical potential of the Flory-Huggins model [72,73] with three-body interactions

$$\hat{\mu}-\hat{\mu}_0=\left(\frac{1}{N}\ln\tilde{\rho}-\ln(1-\tilde{\rho})\right)-\frac{2\tilde{a}\rho}{k_BT}\left(1-\frac{3}{2}c\tilde{\rho}\right), \tag{95}$$

where $N=l/l_0>0$ is the effective association number. The Flory-Huggins model was originally formulated and commonly used for $N\gg1$, to describe thermodynamics of long polymer chains in a monomerlike solvent [72]. However, one may consider N as a phenomenological parameter that is also allowed to be <1. In a certain sense, the parameter N is similar to the fine-lattice discretization parameter ζ, however, in contrast to the fine-lattice discretization model, the lattice spacing l_0 is now fixed, while the molecular volume may change. While at $\zeta\to\infty$ the fine-lattice discretization model is reduced to the van der Waals equation, the limit $N\to\infty$ in the Flory-Huggins model represents the θ point, the limiting phase separation point at zero density and infinite molecular volume. The critical parameters ρ_c and T_c of the model given by Eq. (95) are both functions of N and c,

$$6c(N-1)\rho_c^3+[3c(2-N)-2(N-1)+6c]\tilde{\rho}_c^2-(6c+4)\tilde{\rho}_c+2=0, \tag{96}$$

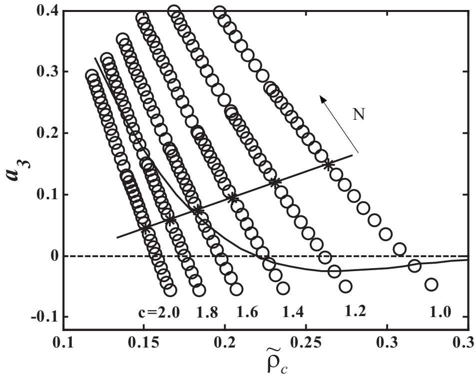

FIG. 20. Parameter a_3 in the Flory-Huggins model with three-body interactions as a function of $\tilde{\rho}_c$ and N. Stars (connected by a solid line) indicate N=1. Solid curve is a guidance for real fluids shown in Fig. 24.

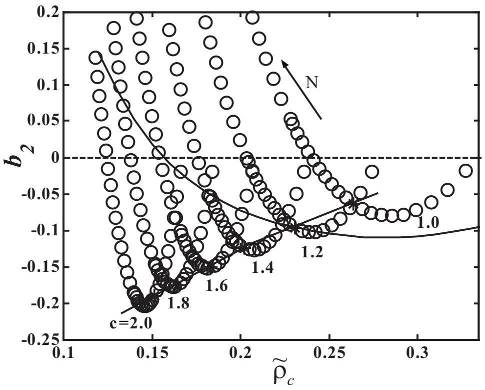

FIG. 21. Asymmetry parameter b_2 in the Flory-Huggins model with three-body interactions as a function of $\tilde{\rho}_c$ and N. Stars, connected by a solid line, indicate $N=1$. Solid curve is a guidance for real fluids shown in Fig. 24.

$$\frac{k_B T_c}{\tilde{a}} = \frac{N\tilde{\rho}_c(1-\tilde{\rho}_c)(2-3c\tilde{\rho}_c)}{1-\tilde{\rho}_c(1-N)}. \tag{97}$$

As shown in Figs. 20 and 21, both a_3 and b_2 start from small negative values, when $N<1$, and generally increase as the molecular volume becomes larger. When $N=1$ and $c=0$, the model is reduced to the symmetric lattice-gas model. When N or c increase, the critical density ρ_c becomes smaller, which means that, generally, a larger molecular volume and stronger three-body interactions increase the phase asymmetry.

VIII. CROSSOVER BETWEEN RECTILINEAR DIAMETER AND "COMPLETE-SCALING" SINGULAR DIAMETER

Since the thermodynamic properties in the critical region are strongly affected by the fluctuations of the order parameter, all mean-field equations of state fail near the critical point. Wyczalkowska *et al.* [74] developed a crossover van der Waals equation which satisfies the scaling theory near the critical point and is reduced to the classical van der Waals equation far away from the critical point. The crossover procedure [49], which execute transformations of the thermodynamic variables in the Helmholtz energy, is based on the renormalization-group theory of critical phenomena [1] and can be, in principle, applied for other, more realistic, equations of state [4]. The quality of crossover transformations used in Ref. [74] is confirmed by excellent agreement between the crossover theory and accurate simulation data for the three-dimensional Ising model with a variety of interaction ranges [38]. However, in Ref. [74] the vapor-liquid asymmetry was incorporated in crossover procedure in the way given by "incomplete scaling." As a result, the second derivative of the chemical potential with respect to temperature was obtained finite at the critical point, the Yang-Yang anomaly was absent, and the singular diameter contained the $|\Delta\hat{T}|^{1-\alpha}$ term only.

In this section we show how the rectilinear diameter affected by fluctuations in the critical region transforms into the singular diameter, splitting in two nonanalytic terms, $\propto|\Delta\hat{T}|^{1-\alpha}$ and $\propto|\Delta\hat{T}|^{2\beta}$, as predicted by complete scaling. Equations (29) and (30) are valid in both mean-field and scaling regimes. Therefore, in order to obtain a crossover equation for $\Delta\hat{\rho}$ one needs crossover expressions for ϕ_1 and ϕ_2. An explicit crossover expression for ϕ_1 in zero field was suggested by Gutkowski *et al.* [75] as an approximation of a more rigorous but implicit result of the crossover theory [38,49,54]:

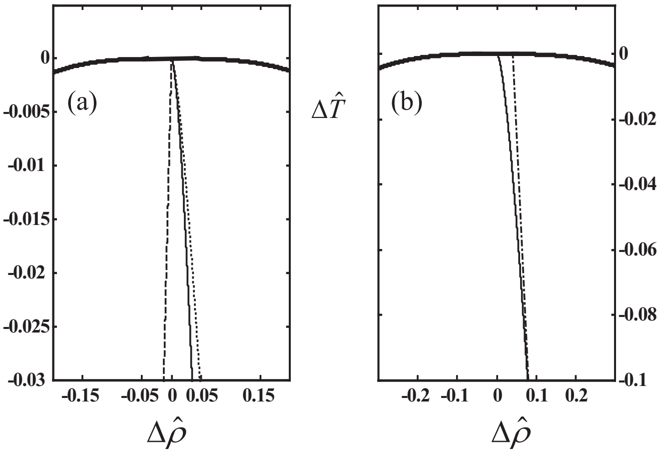

FIG. 22. Crossover diameter of a van der Waals fluid modified by fluctuations with a short interaction range $c_t=1/2$. Thick solid curves are the phase boundary. (a) Two contributions in the singular diameter (solid line): $1-\alpha$ and linear term (dashed line) and 2β (dotted line); (b) crossover between rectilinear diameter (dashed-dotted line) and singular diameter (solid line) in a broader critical region.

$$\phi_1^2 = \left(-\frac{6u_0}{a_0^2}h_2\right)Y^{(2\beta-1)/\theta}, \tag{98}$$

where Y is a crossover function which depends on a dimensionless parameter c_t (inversely proportional to the square of the intermolecular interaction range). The crossover function Y is defined such that at $|\Delta\hat{T}|\gg c_t^{3/2}$ Eq. (98) is reduced to the mean-field expression (50). The scaling limit given by Eq. (8) is recovered at $|\Delta\hat{T}|\ll c_t^{3/2}$ asymptotically close to the critical point.

Crossover behavior of the second scaling density ϕ_2 in the two-phase region cannot be represented by an explicit equation. This behavior was obtained by the numerical integration of the crossover behavior of the isochoric heat capacity for the van der Waals fluid reported in Ref. [74]. In Fig. 22 crossover between the van der Waals rectilinear diameter ($D=2/5$) and complete-scaling singular diameter is shown for a relatively short range of interactions, $c_t=1/2$. It is seen from this figure that the fluctuation-induced shift in the classical van der Waals critical density is mainly controlled by the $|\Delta\hat{T}|^{2\beta}$ nonanalytic term, since the van der Waals value of a_3 is relatively large ($a_3=1/4$).

Finally, in Fig. 23 we show crossover between the classical discontinuity in $(\partial^2\hat{\mu}/\partial\hat{T}^2)_\rho$ and the asymptotic scaling divergence of this derivative for a van der Waals fluid affected by fluctuations with a short range of interactions, c_t

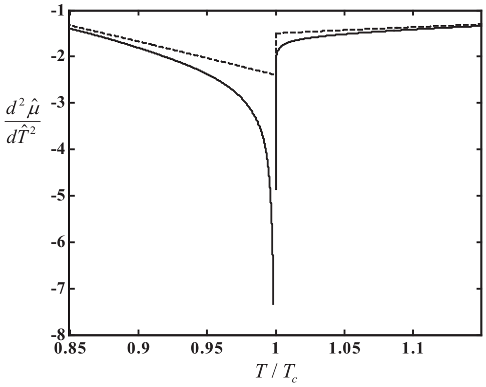

FIG. 23. The second temperature derivative of the chemical potential of a van der Waals fluid modified by fluctuations for a short interaction range, $c_t=1$ (solid line) and its mean-field behavior (dashed line), along the critical isochore as a function of temperature. In the two-phase region $d^2\hat{\mu}/d\hat{T}^2=(d^2\hat{\mu}/d\hat{T}^2)_{\mathrm{cxc}}$, in the one-phase region $d^2\hat{\mu}/d\hat{T}^2=(\partial^2\hat{\mu}/\partial\hat{T}^2)_{\rho=\rho_c}$.

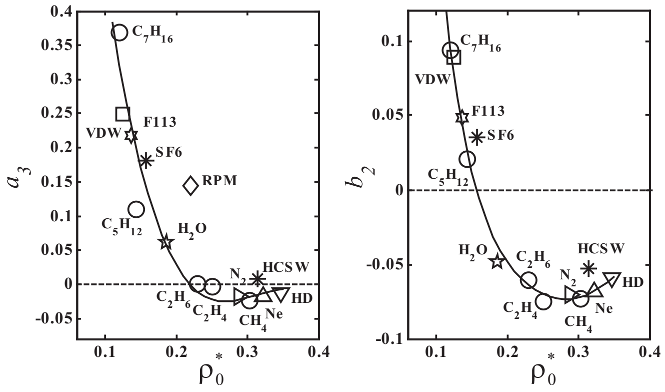

FIG. 24. Complete-scaling asymmetry coefficients a_3 (a) and b_2 (b) versus reduced critical density $\rho^*=\rho_c(8\xi_0^3)$. VDW is a modified-by-fluctuations van der Waals fluid [74] with a short interaction range $[(\rho^*)^{1/3}=0.5]$. HCSW is a simulated hard-core square-well model [41]. For a simulated restrictive primitive model (RPM) [41] $a_3=0.14$ and $b_2=-0.48$ with $\rho^*\simeq 0.22$. The solid curves are given as a guide for the eye.

$=1$. While this divergence is predicted by "complete scaling," in the traditional "incomplete" scaling the classical discontinuity simply disappears in the critical region making $(\partial^2\hat{\mu}/\partial\hat{T}^2)_\rho$ finite at the critical point [74].

IX. DISCUSSION

As early as in 1930s, Eyring [76] discussed the origination of inclinations in vapor-liquid rectilinear diameters. Eyring considered a lattice that thermally expands as the temperature increases. Therefore, the higher the temperature, the lower the average density of the coexisting phases with an inclination of the rectilinear diameter in the right direction, an effect similar to real fluids. In 1972 Widom [6] gave a comprehensive review of vapor-liquid asymmetry near the critical point. Widom showed that in the so-called penetrable-sphere model [16] a nonanalytic term $\propto|\Delta\hat{T}|^{1-\alpha}$ appeared asymptotically close to the critical point. In fact, as it was recently shown [47], the penetrable sphere model has an exact symmetry axis on which the chemical potential is an analytic function of temperature. This is why "incomplete scaling," which predicts a finite $(\partial^2\hat{\mu}/\partial\hat{T}^2)_\rho$ at the critical point and a single leading nonanalytic term, $\propto|\Delta\hat{T}|^{1-\alpha}$, in the "diameter," may be perfectly valid for some specific models.

Our study of the phase asymmetry in various fluids has shown that the nature of the asymmetry can be properly understood only in the framework of "complete scaling" formulated by Fisher and co-workers [19–21]. Generally, in the critical region the rectilinear diameter splits into two singular terms, namely $\propto|\Delta\hat{T}|^{1-\alpha}$ and $\propto|\Delta\hat{T}|^{2\beta}$. The $|\Delta\hat{T}|^{1-\alpha}$ term originates from a coupling between the symmetric order parameter and entropy, while the $|\Delta\hat{T}|^{2\beta}$ is caused by coupling between the order parameter and molecular volume. In the mean-field regime both nonanalytic terms converge into the rectilinear diameter predicted by classical equations of state.

In the diameters of some fluids, such as SF_6, $C_2F_3Cl_3$, and n-C_7H_{16}, the $|\Delta\hat{T}|^{2\beta}$ term dominates (a_3 is relatively large and positive) while in many other fluids, such as HD, Ne, N_2, and CH_4, the two singular contributions in diameter largely compensate each other (a_3 is small and negative, b_2 is also negative), creating an illusion of rectilinear diameter even relatively close to the critical point. In Fig. 24 the two asymmetry coefficients are plotted against the normalized critical density $\rho_0^*=\rho_c(8\xi_0^{+3})$ (which also may be defined as reduced "interaction volume"), where the amplitude of the correlation length ξ_0^+ (representing the range of interactions) is obtained from the heat-capacity amplitude A_0^+ through the two-scale factor of universality, $A_0^+\rho_c\xi_0^3\simeq 0.171$ [2,18]. A general trend in the two sources of asymmetry is clear: the $|\Delta\hat{T}|^{2\beta}$ term, predicted by complete scaling, is a dominant contribution into the singular diameter if the molecular size and/or interaction-range ratio is large. Apparently, ξ_0 does not increase significantly with increase of molecular volume in simple fluids [3]. Thus, when the molecular size is large, the $|\Delta\hat{T}|^{2\beta}$ term is dominant. For fluids with small molecules, the major contribution in the "diameter" is given by a coupling between the order parameter and entropy. However, when the molecular size becomes very small, this contribution vanishes. In particular, for ^{3}He the parameter $\rho_0^*\simeq 1.37/A_0^+\simeq 0.4$ [54] and, in accordance to the guidance given by Fig. 24, the parameter a_3 is expected to be zero. The parameter b_2 is also expected to be very small and negative, but not vanishing, since the estimated slope of the "diameter" in ^{3}He is about 0.02 [10]. The same order-of-magnitude value is expected for b_2, when estimated with the mean-field expression (68).

One can see in Fig. 24 that both a_3 and b_2 depend strongly on the molecular volume and thus on the molecular polarizability. For real fluids these two asymmetry coefficients are, in principle, independent but somehow correlated. In particular, for the van der Waals fluid a_3 and b_2, given by Eq. (80), are not independent and can be expressed through each other with Eqs. (66) and (67) at the condition $\hat{\mu}_{21}=0$. One can also learn from our studies of various mean-field equations of state that depending on the interplay between three-body interactions and molecular size, the contribution associated either with a_3 or with b_2 may be eliminated.

A simple physical interpretation of the "complete-scaling" coefficient a_3 is obtained for liquid binary mixtures by Cerdeiriña *et al.* [77]. It is shown in Ref. [77] that the asymmetry of liquid-liquid coexistence in terms of mole fractions, like the vapor-liquid asymmetry in terms of molar densities, originates from two different sources: one is associated with a correlation between entropy and concentration and generates a nonanalytic term $\propto|\Delta\hat{T}|^{1-\alpha}$, whereas another source is the difference between the molecular volumes of the solvent and of the solute. This difference generates a lower-order, and thus more significant, nonanalytic term $\propto|\Delta\hat{T}|^{2\beta}$. By analyzing coexisting curves of liquid solutions of nitrobenzene in a series of hydrocarbons (from *n*-pentane to *n*-hexadecane), Cerdeiriña *et al.* have observed that the amplitude of the $|\Delta\hat{T}|^{2\beta}$ term near-linearly correlates with the solvent and/or solute molecular-volume ratio and vanishes when the molecular volumes are equal.

X. SUMMARY

In this paper, the nature of asymmetry in fluid criticality has been investigated in the framework of "complete scaling." We have simplified the formulation of "complete scaling" to a form with only two independent mixing coefficients a_3 and b_2 and made it convenient for practical use by a proper choice of the critical entropy $S_c=\rho_c^{-1}(\partial P/\partial T)_{h_1=0,c}$. We have also developed a method to obtain the asymmetry coefficients a_3 and b_2, responsible for two different sources of the asymmetry, from mean-field equations of state. By analyzing several classical equations of state, we have found that the vapor-liquid asymmetry in fluids near the critical point can be controlled by molecular parameters, such as the molecular size and the relative strength of three-body interactions. By combining vapor-liquid coexistence and heat-capacity data, we have unambiguously proved the experimental and simulation evidence of "complete scaling." A number of systems, eleven real fluids and two simulated models (the hard-core square-well fluid and the restricted primitive model), have been analyzed. The asymmetry in fluid criticality originates from a coupling between the symmetric order parameter and entropy which produces a term $\propto|\Delta\hat{T}|^{1-\alpha}$ in the coexistence-curve diameter and from a coupling between the order parameter and molecular volume which produces a term $|\Delta\hat{T}|^{2\beta}$. The ratio of molecular size to the range of interactions plays a crucial role in the asymmetry of fluids. In fluids with relatively small molecules and relatively large range of interactions the asymmetry is small and even may be negligible (^{3}He). Another important conclusion of our study is that, since near-critical vapor-liquid asymmetry is completely determined by the Ising-model critical exponents, there is no need, at least in practice, for a special renormalization-group theoretical treatment of the asymmetric fluid criticality.

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