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Principle of isomorphism and complete scaling for binary-fluid criticality

Jingtao Wang,[1,*] Claudio A. Cerdeiriña,[2] Mikhail A. Anisimov,[1,†] and Jan V. Sengers[1]
[1]*Department of Chemical & Biomolecular Engineering and Institute for Physical Science & Technology, University of Maryland, College Park, Maryland 20742, USA*
[2]*Departamento de Física Aplicada, Universidad de Vigo, Ourense 32004, Spain*

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The extension of the principle of critical-point universality to binary fluid mixtures, known as isomorphism of critical phenomena, has been reformulated in terms of complete scaling, a concept that properly matches asymmetric fluid-phase behavior with the symmetric Ising model. The controversial issue of the proper definition of the order parameter in binary fluid mixtures is clarified. We show that asymmetry of liquid-liquid coexistence in terms of mole fractions originates from two different sources: one is associated with a correlation between concentration and entropy fluctuations, whereas the other source is the correlation between concentration and density fluctuations. By analyzing the coexistence curves of liquid solutions of nitrobenzene in a series of hydrocarbons (from *n*-pentane to *n*-hexadecane), we have separated these two sources of asymmetry and found that the leading nonanalytical contribution to the asymmetry correlates linearly with the solute-solvent molecular-volume ratio. Other thermodynamic consequences of complete scaling for binary mixtures, such as an analog of the Yang-Yang anomaly in the behavior of the heat capacity and a curvature correction to the interfacial tension, are also discussed.

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I. INTRODUCTION

It is commonly accepted that the critical behavior of all fluids, simple and complex, belongs to the universality class of the Ising model (in which the order parameter is either a scalar or a one-component vector [1]). The Ising model, reformulated for the vapor-liquid transition in one-component fluids, is known as the lattice-gas model [2–4]. The lattice-gas model in turn can also be used to describe the liquid-liquid separation in incompressible binary mixtures or the order-disorder transition in binary alloys [5]. The critical behavior of systems with short-range interactions is affected by diverging fluctuations of the order parameter. Within a certain universality class the critical behavior in terms of selected theoretical variables is universal. Moreover, the universal critical behavior is symmetric with respect to the sign of the order parameter. The well-known vapor-liquid asymmetry in real fluids results from relations between the theoretical and the actual "physical" (experimentally defined) variables. The extension of critical-point universality to binary fluids exhibiting a variety of asymmetric fluid-phase equilibria is known as isomorphism of critical phenomena [6–8]. In terms of practical thermodynamic variables, the observed asymmetric critical behavior of fluid mixtures is strongly system dependent. Universality (isomorphic behavior) can be revealed only by transforming the physical (asymmetric) thermodynamic space into the theoretical (symmetric) space.

In this paper the principle of isomorphism is reformulated in terms of complete scaling, a concept that properly matches asymmetric fluid-phase behavior with the symmetric Ising model [9–13]. We try to demystify a controversial issue regarding the proper definition of the order parameter for binary fluid mixtures that has been the subject of prolonged discussions for decades. In general, none of the physical density-like variables can be uniquely identified with the order parameter. Our paper is based on the assumption that liquid mixtures belong to the universality class of Ising-like systems with known theoretical values of the critical exponents for the asymptotic (symmetric) behavior of the coexistence curves. We then show how deviations from asymptotic critical behavior can be incorporated in a systematic way through the mixing of all field variables. Specifically, we show that the asymmetry of liquid-liquid coexistence in binary mixtures in terms of mole fractions originates from two different sources: one is associated with the correlation between concentration and entropy fluctuations, whereas the other is a correlation between concentration and density fluctuations. These two sources of asymmetry generate in first approximation two nonanalytic terms in the average of the mole fractions for the two coexisting phases, known as the coexistence-curve diameter. Incorporating these two sources of asymmetry enables us to significantly enhance the range and quality of the theoretical representation of coexistence curves and coexistence-curve diameters. Moreover, by analyzing the coexistence curves of liquid solutions of nitrobenzene in a series of hydrocarbons (from *n*-pentane to *n*-hexadecane), we have separated these two sources of asymmetry and found that both nonanalytical contributions to the asymmetry correlate with the solvent-solute molecular-volume ratio. Other important thermodynamic consequences of complete scaling for binary mixtures, namely, an analog of the so-called Yang-Yang anomaly in the behavior of the heat capacity and a curvature correction to the interfacial tension, are also discussed.

The paper is organized as follows. First, in Sec. II, we introduce universal relations between theoretical scaling

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[*] Present address: School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072, People's Republic of China

[†] Author to whom correspondence should be addressed. anisimov@umd.edu

fields and scaling densities. The relations are symmetric with respect to the sign of the strongly fluctuating scaling density known as the order parameter. In Sec. III we briefly discuss Fisher's complete scaling for one-component fluids, a new scaling formulation for the relationships between the theoretical scaling fields and the physical field variables. Then, by following Cerdeiriña *et al.* [13], we extend complete scaling to binary fluids in Sec. IV. This extension is elaborated in more detail in Sec. V for incompressible binary liquid solutions. In Sec. VI we specifically discuss one of the most important consequences of complete scaling, namely, a nonanalytic behavior of the coexistence-curve diameter in binary liquid mixtures, while in Sec. VII we provide experimental evidence for the validity of complete scaling by analyzing liquid-liquid phase equilibria in solutions of nitrobenzene with *n*-alkanes. In Sec. VIII we consider other consequences of complete scaling that could be tested experimentally in binary liquid solutions, namely, the analog of the Yang-Yang anomaly in the behavior of the heat capacity and the divergence of Tolman's length, a curvature correction to the interfacial tension. Finally, in Sec. IX the nature of the binary-liquid asymmetry and the proper definition of the order parameter in binary liquid solutions are discussed.

II. SYMMETRIC SCALING AND UNIVERSALITY

The fluctuation-induced nonanalytic critical behavior 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 of an appropriate field-dependent thermodynamic potential, which is defined as a function exhibiting a minimum at equilibrium with respect to a variation of the order parameter. The differential of the third field is

$$dh_3 = \phi_1 dh_1 + \phi_2 dh_2. \tag{1}$$

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

$$h_3 \approx |h|_2^{2-\alpha} f^{\pm}\left(\frac{h_1}{|h|_2^{2-\alpha-\beta}}\right), \tag{2}$$

where $f^{\pm}$ is a scaling function and the superscript ± refers to $h_2 > 0$ and $h_2 < 0$, respectively. Here and below $\approx$ means asymptotically equal, while $\simeq$ means approximately equal. The form of the scaling function is universal; however, it contains two thermodynamically independent (but system-specific) 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 universality class. The Ising values for $\alpha \simeq 0.109$ and $\beta \simeq 0.326$ are well established theoretically and confirmed experimentally [14–20]. The two corresponding Ising amplitudes $\hat{A}_0$ and $\hat{B}_0$ are determined by the asymptotic power-law behavior of the two scaling densities in zero ordering field ($h_1 = 0$):

$$\phi_1 = \left(\frac{\partial h_3}{\partial h_1}\right)_{h_2} \approx \pm \hat{B}_0 |h_2|^{\beta} \quad (h_2 < 0), \tag{3}$$

$$\phi_2 = \left(\frac{\partial h_3}{\partial h_2}\right)_{h_1} \approx \frac{\hat{A}_0^{\pm}}{1-\alpha} h_2 |h_2|^{-\alpha}, \tag{4}$$

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

$$\chi_1 = \left(\frac{\partial \phi_1}{\partial h_1}\right)_{h_2} \approx \hat{\Gamma}_0^{\pm} |h_2|^{-\gamma}, \tag{5}$$

$$\chi_2 = \left(\frac{\partial \phi_2}{\partial h_2}\right)_{h_1} \approx \hat{A}_0^{\pm} |h_2|^{-\alpha}, \tag{6}$$

$$\chi_{12} = \left(\frac{\partial \phi_1}{\partial h_2}\right)_{h_1} \approx \beta \hat{B}_0 \frac{|h_2|^{\beta}}{h_2} \quad (h_2 < 0), \tag{7}$$

where the critical exponent $\gamma = 2 - \alpha - 2\beta \simeq 1.239$ and the Ising critical amplitude $\hat{\Gamma}_0^{\pm}$ is related to $\hat{B}_0$ and $\hat{A}_0^{\pm}$ through universal ratios $\alpha \hat{\Gamma}_0^{+} \hat{A}_0^{+} / \hat{B}_0^2 \simeq 0.0581$, $\hat{\Gamma}_0^{+} / \hat{\Gamma}_0^{-} \simeq 4.8$, and $\hat{A}_0^{+} / \hat{A}_0^{-} \simeq 0.523$ [21]. While the superscript ± refers to the states at $h_2 > 0$ and $h_2 < 0$, the prefactor ± in Eq. (3) refers to the two branches of the order parameter corresponding to the $h_1 > 0$ and $h_1 < 0$ sides (in the limit $h_1 = 0$), respectively. The field-dependent potential h_3 is symmetric with respect to the sign of the ordering field h_1 and, hence, to the sign of the order parameter ϕ_1.

In the mean-field approximation, with $\alpha = 0$ and $\beta = 1/2$, Eq. (2) reduces to the asymptotic Landau expansion [22],

$$-h_3 \approx \frac{1}{2} a_0 h_2 \phi_1^2 + \frac{1}{24} u_0 \phi_1^4 - h_1 \phi_1, \tag{8}$$

where a_0 and u_0 are mean-field system-dependent amplitudes. In the lattice-gas model the ordering field h_1 is associated with the chemical potential μ, the thermal field h_2 is associated with the temperature T, and the order parameter is associated with the molecular density ρ, while h_3 is associated with the pressure P. In both the scaling regime and the mean-field approximation, the thermodynamic properties of the lattice gas are symmetric with respect to the sign of the order parameter.

III. COMPLETE SCALING FOR ONE-COMPONENT FLUIDS

While the lattice gas has perfect symmetry with respect to the sign of the order parameter, real fluids approach such symmetry only asymptotically. In order to apply the scaling theory given by Eq. (2) to real fluids and fluid mixtures, one needs to establish relationships between the theoretical scaling variables and the physical thermodynamic variables. Since the early 1970s, it has been postulated that, for the vapor-liquid critical point in one-component fluids, the two independent theoretical scaling fields h_1 and h_2 are both linear combinations of two independent physical fields, namely, the chemical potential μ and the temperature T, while the third (dependent) field follows as $h_3=(P-P_{\mathrm{cxc}})/\rho_c k_B T_c$, where P_{cxc} is the pressure at vapor-liquid coexistence, which coincides with the condition $h_1=0$ [23]. This postulate can be called “incomplete scaling” [12]. Therefore, in incomplete scaling $-h_3$ is the critical part of the grand thermodynamic potential $\Omega=-PV$ per unit volume V. Correspondingly, the critical part of the Helmholtz energy A per unit volume, $\Delta\hat{A}=\Delta A/Vk_B T_c$, is defined by a Legendre transformation as $\Delta\hat{A}=-h_3+h_1\phi_1$ [24]. Here and below the subscript "c" indicates the values at the critical point, such as the critical molecular density ρ_c or the critical temperature T_c; k_B is Boltzmann’s constant.

Recently, Fisher and co-workers [9–11] have developed a scaling formulation for one-component fluids, known as complete scaling. The major conceptual idea of complete scaling is that asymmetric fluids can be consistently mapped into the symmetric Ising criticality by mixing of all three physical fields $\Delta\hat{\mu}=(\mu-\mu_c)/k_B T_c$, $\Delta\hat{T}=(T-T_c)/T_c$, and $\Delta\hat{P}=(P-P_c)/\rho_c k_B T_c$ into the three theoretical scaling fields h_1, h_2, and h_3.

In linear approximation,

$$h_1=a_1\Delta\hat{\mu}+a_2\Delta\hat{T}+a_3\Delta\hat{P}, \tag{9}$$

$$h_2=b_1\Delta\hat{T}+b_2\Delta\hat{\mu}+b_3\Delta\hat{P}, \tag{10}$$

$$h_3=c_1\Delta\hat{P}+c_2\Delta\hat{\mu}+c_3\Delta\hat{T}. \tag{11}$$

The dependent field h_3 is a homogeneous function of h_1 and h_2 as asymptotically given by Eq. (2). Beyond the asymptotic region [25], or, if the phase-coexistence locus $h_1=0$ exhibits an anomalously strong curvature in terms of the physical fields [26], the linear approximation may be insufficient and appropriate nonlinear terms have to be included.

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

$$\hat{\rho}\equiv\frac{\rho}{\rho_c}=\left(\frac{\partial\hat{P}}{\partial\hat{\mu}}\right)_{\hat{T}},\quad \hat{\rho}\hat{S}\equiv\frac{\rho S}{\rho_c k_B}=\left(\frac{\partial\hat{P}}{\partial\hat{T}}\right)_{\hat{\mu}}. \tag{12}$$

Since the coefficients c_1 and c_2 can be absorbed by making the thermodynamic potential h_3 appropriately dimensionless (by $\rho_c k_B T_c$), such that $c_1=1$ and $c_2=-\hat{\rho}_c=-1$, and the coefficient $c_3=-\hat{\rho}_c\hat{S}_c=-\hat{S}_c$ (in Ref. [12] c_3 was misprinted as $c_3=\hat{S}_c$), one can obtain by applying Eq. (12) to Eqs. (9)–(11) [12]

$$\hat{\rho}=\frac{1+a_1\phi_1+b_2\phi_2}{1-a_3\phi_1-b_3\phi_2}, \tag{13}$$

$$\hat{\rho}\hat{S}=\frac{\hat{S}_c+a_2\phi_1+b_1\phi_2}{1-a_3\phi_1-b_3\phi_2}. \tag{14}$$

While the scaling fields are expressed as linear combinations of the physical fields, the physical densities are nonlinear combinations of the scaling densities. In traditional (incomplete) scaling a_3 and b_3 are assumed to be zero and the physical densities are linear combinations of the scaling densities [7].

As shown by Anisimov and Wang [12], complete scaling can be simplified to a form convenient for practice by using the thermodynamic freedom for a choice of critical-entropy value, which is arbitrary in classical thermodynamics. By adopting $\hat{S}_c=(\partial\hat{P}/\partial\hat{T})_{h_1=0,c}$ one obtains $(\partial\hat{\mu}/\partial\hat{T})_{h_1=0,c}=0$ and

$$a_2+a_3\left(\frac{\partial\hat{P}}{\partial\hat{T}}\right)_{h_1=0,c}=0. \tag{15}$$

Furthermore, with this choice of $\hat{S}_c$, along the path $h_1=0$, $h_2=\Delta\hat{T}(1-b_3a_2/a_3)$ the density of entropy becomes proportional to the weakly fluctuating scaling density $\Delta(\hat{\rho}\hat{S})\approx(1+\hat{S}_c b_3)\phi_2\propto|h_2|^{1-\alpha}$. 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 the asymmetry of fluid criticality. Indeed, as follows from the expansion of Eq. (13), 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, in Ref. [12], the terms containing b_3 were neglected. Moreover, just as $h_1=\Delta\hat{\mu}$ and $h_2=\Delta\hat{T}$ in the symmetric (lattice-gas) approximation, the coefficients a_1 and b_1 can be absorbed in two independent scaling amplitudes in the argument of the scaling function in Eq. (2). Finally, the scaling fields for one-component fluids read

$$h_1=\Delta\hat{\mu}+a_3\left[\Delta\hat{P}-\left(\frac{d\hat{P}}{d\hat{T}}\right)_{\mathrm{cxc,c}}\Delta\hat{T}\right], \tag{16}$$

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

$$h_3=\Delta\hat{P}-\Delta\hat{\mu}-\left(\frac{d\hat{P}}{d\hat{T}}\right)_{\mathrm{cxc,c}}\Delta\hat{T}. \tag{18}$$

Furthermore, by expanding Eqs. (13) and (14) and neglecting all terms of higher order than those linear in $\Delta\hat{T}$, one obtains

$$\Delta\hat{\rho}\simeq(1+a_3)\phi_1+a_3(1+a_3)\phi_1^2+(b_2+b_3)\phi_2 \tag{19}$$

and

$$\Delta(\hat{\rho}\hat{S})\simeq(1+\hat{S}_c b_3)\phi_2. \tag{20}$$

Hence, there are only two independent coefficients that in first approximation control the asymmetry in fluid criticality, namely, a_3 and $b_{\mathrm{eff}}=(b_2+b_3)/(1+\hat{S}_c b_3)$. In Ref. [12], the coefficient b_3 was assumed zero, so that b_{eff} was approximated as $b_{\mathrm{eff}}=b_2$.

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. Since asymptotically ϕ_1^2

$\propto|\Delta\hat{T}|^{2\beta}$ and $\phi_2\propto|\Delta\hat{T}|^{1-\alpha}$, the average of the liquid and vapor densities, ρ' and ρ'', contains two nonanalytic terms, proportional to $|\Delta\hat{T}|^{2\beta}$ and $|\Delta\hat{T}|^{1-\alpha}$, respectively,

$$\Delta\hat{\rho}_{\mathrm{d}}\equiv\frac{\rho'+\rho''}{2\rho_{\mathrm{c}}}-1=D_2|\Delta\hat{T}|^{2\beta}+D_1|\Delta\hat{T}|^{1-\alpha}+\cdots,\quad(21)$$

where the coefficients D_2 and D_1 are proportional to the amplitudes $\hat{B}_0^2$ and $\hat{A}_0^-$ defined by Eqs. (3) and (4) [12]. Since $2\beta\simeq0.652<1-\alpha\simeq0.891$, the first term, which does not exist in the traditional scaling formulation for fluids but emerges from complete scaling, is asymptotically more important than the second one. However, the apparent behavior of the average density depends also on the amplitudes of these terms, which are system dependent. It has been shown [12] that the term $\propto|\Delta\hat{T}|^{2\beta}$ indeed dominates in the average of the coexisting densities for fluids consisting of large molecules, such as *n*-heptane or sulfur hexafluoride, and for ionic fluids.

IV. EXTENSION OF COMPLETE SCALING TO BINARY FLUIDS

The generalization of critical-point universality to binary fluids is known as the principle of isomorphism [6–8]. This principle assumes that a variety of critical phenomena in binary fluids can still be described in a universal way with the same theoretical scaling fields h_1, h_2, and h_3, given by Eq. (2), as in a one-component fluid. The variety of experimentally observed critical behavior in binary fluids is hidden in the relations between the scaling fields and the actual physical fields. The principle of isomorphism was initially formulated in terms of incomplete scaling by the assumption that the two independent scaling fields h_1 and h_2 are linear combinations of the independent physical field variables only, namely, the temperature and the chemical potentials of the two components, while $-h_3$ was assumed to be still the critical part of the grand thermodynamic potential $\Omega=-PV$ per unit volume, just as in a one-component fluid. However, the concept of complete scaling implies that all physical fields, independent and dependent, are to be mixed into the scaling fields. Extended to binary fluids, this concept thus implies that the scaling fields for binary fluids in linear approximation should read [13]

$$h_1=a_1\Delta\hat{\mu}_1+a_2\Delta\hat{T}+a_3\Delta\hat{P}+a_4\Delta\hat{\mu}_{\Delta21},\quad(22)$$

$$h_2=b_1\Delta\hat{T}+b_2\Delta\hat{\mu}_1+b_3\Delta\hat{P}+b_4\Delta\hat{\mu}_{\Delta21},\quad(23)$$

$$h_3=c_1\Delta\hat{P}+c_2\Delta\hat{\mu}_1+c_3\Delta\hat{T}+c_4\Delta\hat{\mu}_{\Delta21},\quad(24)$$

where $\Delta\hat{\mu}_1=(\mu_1-\mu_{1c})/k_BT_c$ with μ_1 being the chemical potential of the solvent conjugate to the molecular density ρ and $\Delta\hat{\mu}_{\Delta21}=(\mu_{\Delta21}-\mu_{\Delta21c})/k_BT_c$ with $\mu_{\Delta21}$ being the solute-solvent chemical potential difference conjugate to the mole fraction x.

The scaling densities are defined in the same way as for one-component fluids:

$$\phi_1=\left(\frac{\partial h_3}{\partial h_1}\right)_{h_2},\quad(25)$$

$$\phi_2=\left(\frac{\partial h_3}{\partial h_2}\right)_{h_1}.\quad(26)$$

Physical density-like properties, namely, the molecular density, the mole fraction, entropy per molecule, entropy per unit volume, and molarity, also known as "partial density" $\rho_2=\rho x$ (number of solute molecules per unit volume) [7] are given by the following thermodynamic relations:

$$x=-\left(\frac{\partial\mu_1}{\partial\mu_{\Delta21}}\right)_{T,P},\quad(27)$$

$$\rho=\left(\frac{\partial P}{\partial\mu_1}\right)_{T,\mu_{\Delta21}},\qquad\rho_2=\rho x=\left(\frac{\partial P}{\partial\mu_{\Delta21}}\right)_{T,\mu_1}.\quad(28)$$

$$S=-\left(\frac{\partial\mu_1}{\partial T}\right)_{\mu_{\Delta21},P},\qquad\rho S=\left(\frac{\partial P}{\partial T}\right)_{\mu_1,\mu_{\Delta21}}.\quad(29)$$

Just as for a one-component fluid, one can assign $c_1=1$ and $c_2=-1$, while $c_3=-\hat{S}_c$ and $c_4=-\hat{\rho}_cx_c=-x_c$.

According to the principle of isomorphism, experimentally observed physical properties, such as osmotic susceptibility, heat capacity, and concentration difference in coexisting phases, asymptotically can still exhibit universal power laws as functions of $\Delta\hat{T}$ with the universal critical exponents introduced by Eqs. (3)–(7) provided that the other physical fields are kept constant. If, instead, a physical density, such as ρ or x, is kept constant, a phenomenon of renormalization of the critical exponents, known as Fisher renormalization [27] may take place depending on the position along the critical line (see details in Refs. [7,8]).

By combining the relations (27)–(29) with Eqs. (22)–(26) one can express all the physical densities of binary fluids through the theoretical scaling densities ϕ_1 and ϕ_2 as

$$x=\frac{x_c+a_4\phi_1+b_4\phi_2}{1+a_1\phi_1+b_2\phi_2},\quad(30)$$

$$\hat{\rho}=\frac{1+a_1\phi_1+b_2\phi_2}{1-a_3\phi_1-b_3\phi_2},\quad(31)$$

$$\hat{\rho}x=\frac{x_c+a_4\phi_1+b_4\phi_2}{1-a_3\phi_1-b_3\phi_2},\quad(32)$$

$$\hat{S}=\frac{\hat{S}_c+a_2\phi_1+b_1\phi_2}{1+a_1\phi_1+b_2\phi_2},\quad(33)$$

$$\hat{\rho}\hat{S}=\frac{\hat{S}_c+a_2\phi_1+b_1\phi_2}{1-a_3\phi_1-b_3\phi_2}.\quad(34)$$

Since the mole fraction, entropy, molecular density, and their products appear to be nonlinear combinations of the scaling densities, neither of these experimentally measured properties can serve as the order parameter for binary fluids. The actual behavior of these properties depends on the values of the mixing coefficients which, in turn, depend parametrically on the position of the critical point along the critical locus [7]. In the one-component limit the coefficients a_4, b_4, and c_4 vanish, being proportional to x_c [7], while a_3 and b_3 vanish in the incompressible limit.

V. INCOMPRESSIBLE BINARY LIQUIDS

An interesting and practically important case is the limit of an incompressible binary liquid mixture. In an incompressible mixture the total volume will not fluctuate. However, since in asymmetric liquid mixtures the molecular volumes of the individual components may be different, concentration fluctuations may be accompanied by fluctuations in the molecular density (number of molecules per unit volume), even in the incompressible limit. In this limit the coefficients a_3 and b_3 in the scaling fields h_1 and h_2 vanish, while the number of the independent variables reduces to 2, just as for one-component fluids. Moreover, since in the symmetric (incompressible binary lattice model) approximation $h_1=\Delta\hat{\mu}_{\Delta 21}$ and $h_2=\Delta\hat{T}$, the coefficients a_4 and b_1 can be absorbed in two independent scaling amplitudes. Equations (22)–(24) now become

$$h_1 = \Delta\hat{\mu}_{\Delta 21} + a_1\Delta\hat{\mu}_1 + a_2\Delta\hat{T}, \qquad (35)$$

$$h_2 = \Delta\hat{T} + b_2\Delta\hat{\mu}_1 + b_4\Delta\hat{\mu}_{\Delta 21}, \qquad (36)$$

$$h_3 = \Delta\hat{P} - \Delta\hat{\mu}_1 - \hat{S}_c\Delta\hat{T} - x_c\Delta\hat{\mu}_{\Delta 21}. \qquad (37)$$

Note that the coefficient c_1 in the dependent field h_3 in the incompressible limit remains $c_1=1$, so that the density in this limit still can be defined thermodynamically by Eq. (28). Furthermore, with the choice of the critical-entropy value as $\hat{S}_c=-(\partial\hat{\mu}_1/\partial\hat{T})_{h_1=0,c}$ we obtain the conditions $(\partial\hat{\mu}_{\Delta 21}/\partial\hat{T})_{h_1=0,c}=0$ and

$$a_2 + a_1\left(\frac{\partial\hat{\mu}_1}{\partial\hat{T}}\right)_{h_1=0,c} = 0. \qquad (38)$$

The scaling fields finally become

$$h_1 = \Delta\hat{\mu}_{\Delta 21} + a_1\left[\Delta\hat{\mu}_1 - \left(\frac{d\hat{\mu}_1}{d\hat{T}}\right)_{\text{cxc,c}}\Delta\hat{T}\right], \qquad (39)$$

$$h_2 = \Delta\hat{T} + b_4\Delta\hat{\mu}_{\Delta 21} + b_2\Delta\hat{\mu}_1, \qquad (40)$$

$$h_3 = \Delta\hat{P} - \Delta\hat{\mu}_1 - x_c\Delta\hat{\mu}_{\Delta 21} + \left(\frac{d\hat{\mu}_1}{d\hat{T}}\right)_{\text{cxc,c}}\Delta\hat{T}. \qquad (41)$$

On comparing Eqs. (39)–(41) with Eqs. (16)–(18), we see that for an incompressible liquid mixture at constant pressure $\Delta\hat{P}$, the fields h_1, h_2, and h_3 are analogous to the fields h_1, h_2, and $-h_3$ of a one-component fluid with $\hat{\mu}_{\Delta 21}$ and $\hat{\mu}_1$ playing the role of $\hat{\mu}$ and $\hat{P}$ and with the coefficients a_1, b_4, and b_2 playing the same roles as the asymmetry coefficients a_3, b_2, and b_3 in Eqs. (16) and (17). Correspondingly, in the incompressible limit the physical density-like variables become

$$\hat{\rho} = 1 + a_1\phi_1 + b_2\phi_2, \qquad (42)$$

$$x = \frac{x_c + \phi_1 + b_4\phi_2}{1 + a_1\phi_1 + b_2\phi_2} = (x_c + \phi_1 + b_4\phi_2)\hat{\rho}^{-1}, \qquad (43)$$

$$\hat{\rho}x = x_c + \phi_1 + b_4\phi_2, \qquad (44)$$

and, by expanding Eq. (33) with the constraint given by Eq. (38),

$$\hat{S} \simeq \hat{S}_c + (1 - \hat{S}_c b_2)\phi_2. \qquad (45)$$

Interestingly, in the incompressible limit the density, molarity (partial density), and entropy in first approximation become linear combinations of the scaling densities, while the mole fraction does not. Therefore, by taking the difference of the densities or molarities of the two coexisting phases one can obtain the symmetric behavior of the order parameter ϕ_1 in incompressible binary liquids as given by Eq. (3). However, the mole-fraction difference of the coexisting liquid phases is still affected by the asymmetric terms in the density since, as follows from Eq. (43),

$$x' - x'' = \frac{\hat{\rho}' + \hat{\rho}''}{\hat{\rho}'\hat{\rho}''}\phi_1. \qquad (46)$$

Equation (43) for the mole fraction of an incompressible liquid mixture is analogous to Eq. (13) for the density of a one-component fluid with a_1, b_2, and b_4 serving the same roles for liquid-liquid asymmetry as a_3, b_3, and b_2 for vapor-liquid asymmetry. For one-component fluids, the coefficient b_3 cannot be determined from leading asymmetry terms in vapor-liquid coexistence. However, for incompressible binary liquids, the analogous coefficient b_2 can be determined as the leading asymmetry coefficient for the molecular density in accordance with Eq. (42). This is why we shall not neglect this coefficient in further considerations. However, as for one-component fluids [12], we do neglect the higher-order terms of order $b_2\phi_1\phi_2$ and $b_4b_2\phi_2^2$, while expanding Eq. (43), and approximate the thermal field h_2 at $h_1=0$ as

$$h_2 = \Delta\hat{T}\left(1 - b_2\frac{a_2}{a_1}\right) \simeq \Delta\hat{T}, \qquad (47)$$

since the prefactor $1-b_2a_2/a_1\simeq 1$ can be absorbed in an appropriate critical amplitude. Real binary liquids are weakly compressible. However, since experiments on liquid-liquid equilibria are usually conducted at essentially constant (in practice, saturation) pressure, the terms $a_3\Delta\hat{P}$ and $b_3\Delta\hat{P}$ in the expression (22) for h_1 and the expression (23) for h_2 can be neglected for weakly compressible liquid mixtures as well. In a completely symmetric incompressible binary liquid mixture (fully equivalent to the lattice-gas model) a_1, b_2, and b_4 vanish, while the order parameter is solely associated with the mole fraction x. Correspondingly, the ordering scaling field h_1 then becomes $\Delta\hat{\mu}_{\Delta 21}$, while the critical part of the thermodynamic potential is simply equal to $\Delta\hat{\mu}_1$. In the remainder of this paper we shall be specifically concerned with weakly compressible liquid mixtures.

VI. SINGULAR DIAMETER IN BINARY LIQUID MIXTURES

As demonstrated by Anisimov and Wang [12], the scaling fields, given by Eqs. (16)–(18), yield for the density of the two coexisting phases in one-component fluids an expression of Eq. (19) in terms of $\Delta\hat{T}$ (assuming $b_3=0$):

$$\begin{aligned}\Delta\hat{\rho} \equiv \hat{\rho} - 1 &\simeq (1+a_3)\phi_1 + a_3(1+a_3)\phi_1^2 + b_2\phi_2 + \cdots \\ &= \pm B_0|\Delta\hat{T}|^{\beta} + D_2|\Delta\hat{T}|^{2\beta} + D_1|\Delta\hat{T}|^{1-\alpha} + D_0|\Delta\hat{T}| + \cdots,\end{aligned} \tag{48}$$

with

$$B_0 = (1+a_3)\hat{B}_0, \tag{49}$$

$$D_2 = \frac{a_3}{1+a_3}B_0^2, \tag{50}$$

and

$$D_1|\Delta\hat{T}|^{1-\alpha} + D_0|\Delta\hat{T}| \simeq - b_2\left(\frac{A_0^-}{(1-\alpha)}|\Delta\hat{T}|^{1-\alpha} - \hat{B}_{\rm cr}|\Delta\hat{T}|\right). \tag{51}$$

In Eq. (51) $A_0^- = \hat{A}_0^-$ is the amplitude of the asymptotic power law for the dimensionless isochoric heat capacity (per molecule) $\hat{C}_V = C_V/k_{\rm B}$ at $\rho=\rho_{\rm c}$ in the two-phase region and $\hat{B}_{\rm cr} = B_{\rm cr}/k_{\rm B}$ a fluctuation-induced analytical background contribution to $\hat{C}_V$ [12]:

$$\hat{C}_V(\rho=\rho_{\rm c}) \approx A_0^-|\Delta\hat{T}|^{-\alpha} - \hat{B}_{\rm cr}. \tag{52}$$

As shown in the preceding section, the behavior of binary liquid mixtures near a critical point of mixing at constant pressure is isomorphic to the critical behavior of one-component fluids near the vapor-liquid critical point with the pressure $\hat{P}$ replaced by the chemical potential $\hat{\mu}_1$ of the solvent, the chemical potential $\hat{\mu}$ replaced by the solute-solvent chemical-potential difference $\hat{\mu}_{\Delta 21}$, the molecular density $\hat{\rho}$ replaced by the molecular fraction $\hat{x}$, and the coefficients a_3, b_2, and b_3 replaced by a_1, b_4, and b_2, respectively. It thus follows that the solute concentration $\hat{x}$ in the two coexisting liquid phases has a temperature expansion of Eq. (43) analogous to Eq. (48) which, after neglecting all terms of higher order than linear, becomes

$$\begin{aligned}\Delta\hat{x} \equiv \hat{x} - 1 &\simeq \frac{1-x_{\rm c}a_1}{x_{\rm c}}\phi_1 + a_{\rm eff}\phi_1^2 + b_{\rm eff}\phi_2 \simeq \pm B_0|\Delta\hat{T}|^{\beta} \\ &\quad + D_2|\Delta\hat{T}|^{2\beta} + D_1|\Delta\hat{T}|^{1-\alpha} + D_0|\Delta\hat{T}|,\end{aligned} \tag{53}$$

where

$$D_2 = a_{\rm eff}B_0^2, \tag{54}$$

$$a_{\rm eff} = -\frac{a_1}{x_{\rm c}(1-x_{\rm c}a_1)}, \tag{55}$$

$$b_{\rm eff} = \frac{b_4 - x_{\rm c}b_2}{x_{\rm c}(1-\hat{S}_{\rm c}b_2)}, \tag{56}$$

and

$$D_1|\Delta\hat{T}|^{1-\alpha} + D_0|\Delta\hat{T}| \simeq - b_{\rm eff}\left(\frac{A_0^-}{(1-\alpha)}|\Delta\hat{T}|^{1-\alpha} - \hat{B}_{\rm cr}|\Delta\hat{T}|\right). \tag{57}$$

In Eq. (57) $A_0^- = \hat{A}_0^-(1-\hat{S}_{\rm c}b_2)(1-b_2a_2/a_1)^{1-\alpha}$ is now the "physical" amplitude of the fluctuation-induced singular contribution to the dimensionless molecular isobaric heat capacity $\hat{C}_{P,x} = C_{P,x}/k_{\rm B}$ (per molecule) at $x=x_{\rm c}$ in the two-phase region and $\hat{B}_{\rm cr} = B_{\rm cr}/k_{\rm B}$ the fluctuation-induced analytical background contribution:

$$\hat{C}_{P,x}(x=x_{\rm c}) \approx A_0^-|\Delta\hat{T}|^{-\alpha} - \hat{B}_{\rm cr}. \tag{58}$$

It follows from Eq. (53) that the difference $x'-x''$ between the concentrations of the solute along the two sides of the phase boundary varies asymptotically as

$$\Delta_{\rm cxc}\hat{x} \equiv \frac{x'-x''}{2x_{\rm c}} \approx B_0|\Delta\hat{T}|^{\beta}, \tag{59}$$

with

$$B_0 = \hat{B}_0\frac{1-x_{\rm c}a_1}{x_{\rm c}}\left(1 - b_2\frac{a_2}{a_1}\right)^{\beta}. \tag{60}$$

Asymmetry in first approximation does not affect the asymptotic power-law behavior of the concentration difference $(x'-x'')/2x_{\rm c}$ since, as follows from Eqs. (42), (43), and (46), the first nonasymptotic correction associated with asymmetry is almost linear, proportional to $\pm a_1^2B_0^3|\Delta T|^{3\beta}$. But it does affect the asymptotic behavior of the coexistence-curve diameter $\hat{x}_{\rm d} \equiv (x'+x'')/2x_{\rm c}$:

$$\begin{aligned}\Delta\hat{x}_{\rm d} \equiv \hat{x}_{\rm d} - 1 &\simeq a_{\rm eff}B_0^2|\Delta\hat{T}|^{2\beta} \\ &\quad - b_{\rm eff}\left(\frac{A_0^-}{(1-\alpha)}|\Delta\hat{T}|^{1-\alpha} - \hat{B}_{\rm cr}|\Delta\hat{T}|\right).\end{aligned} \tag{61}$$

The term proportional to $|\Delta\hat{T}|^{1-\alpha}$ in Eq. (61) is known to arise from a coupling between concentration fluctuations and entropy fluctuations [7,28]. The term proportional to $|\Delta\hat{T}|^{2\beta}$ accounts for the mixing of $\hat{\mu}_{\Delta 21}$ and $\hat{\mu}_1$ in the expression (39) for the ordering field h_1 and, hence, arises from a coupling between concentration fluctuations and density fluctuations. In fact, experimental data for liquid-liquid coexistence-curve diameters have called for the presence of a term proportional to $|\Delta\hat{T}|^{2\beta}$, but in the past the appearance of such a term was attributed to a wrong choice for the order parameter [19,29–31]. We now see that this term is a direct consequence of complete scaling.

TABLE I. Critical parameters and amplitudes for binary liquid mixtures of nitrobenzene with n-alkanes; σ is the standard deviation of a fit of Eq. (59) to the experimental data.

System	x_c (alkane)	T_c (K)	v_{alk}/v_{NB}	B_0	10σ
NB+C_5 [34]	0.610	297.10	1.12	1.14	0.02
NB+C_6 [32]	0.572	293.13	1.28	1.32	0.03
NB+C_7 [32]	0.529	291.94	1.44	1.47	0.02
NB+C_8 [33]	0.495	293.05	1.59	1.58	0.02
NB+C_{10} [34]	0.425	295.96	1.91	1.84	0.03
NB+C_{11} [35]	0.395	298.01	2.07	2.02	0.03
NB+C_{12} [36]	0.369	300.37	2.22	2.07	0.04
NB+C_{13} [37]	0.357	303.00	2.38	2.14	0.04
NB+C_{14} [38]	0.324	304.94	2.54	2.22	0.05
NB+C_{16} [39]	0.284	309.69	2.86	2.39	0.06

VII. EXPERIMENTAL CONFIRMATION OF COMPLETE SCALING FOR BINARY LIQUID MIXTURES

Experimental evidence for complete scaling in binary liquid solutions was recently presented by Cerdeiriña *et al.* [13]. They considered nitrobenzene+n-alkane mixtures so as to study the nature of asymmetry in liquid-liquid equilibria as a function of the number of carbons in the n-alkanes. Specifically, they fitted the experimental data for the coexistence curve, retaining only the first two asymmetric terms in the expansion (53), using the coefficients D_2 and D_1 as adjustable coefficients. They found that with increasing number of carbon atoms the term proportional to $|\Delta\hat{T}|^{2\beta}$ became more and more dominant, with the asymmetry coefficient originating from complete scaling being controlled by the molecular volume of the n-alkanes. Here we present an analysis in terms of the more complete expansion (61), retaining the theoretically predicted correlation between the $|\Delta\hat{T}|^{1-\alpha}$ and $|\Delta\hat{T}|$ terms through the critical behavior of the two-phase heat capacity.

We have analyzed the mole fractions of the two coexisting liquid phases in the range $3\times10^{-4}<|\Delta\hat{T}|<1\times10^{-2}$ to exclude data very close to the critical temperature that may be affected by uncertainties in the critical parameters and data further away from the critical temperature that may be affected by higher-order terms in the expansion. The critical parameters (adopted from the literature [32–39]), the n-alkane–nitrobenzene molecular-volume ratios v_{alk}/v_{NB} (calculated), and the asymptotic amplitudes B_0, obtained from fitting $(x'-x'')/2x_c$ to Eq. (59), are presented in Table I. With increase of the molecular volume ratio, the critical mole fraction of n-alkane decreases significantly, while the amplitude B_0 increases, as shown in Fig. 1.

The observation that the difference of the concentrations along the two sides of the liquid-liquid phase boundary satisfies the asymptotic power law (59) is not new and has been well established in the literature. In a recent study of the coexistence curve of the n-heptane+nitrobenzene mixture, Fameli and Balzarini observed increasing deviations from the power law (59) toward larger values of the effective exponent of the coexistence curve very close to T_c (at $|\Delta\hat{T}|<10^{-4}$, the range that we avoid) [40]. There may be various reasons for these deviations; however, one can note that a similar effect of shifting effective exponents toward their "classical" values was observed in one-component fluids [41] and, most likely, was caused by gravity. Nitrobenzene and n-heptane have a significant difference in mass densities (about 0.52 $\mathrm{g/cm^3}$) and the data close to T_c might be sensitive to gravity. Another explanation of the effect of shifting the effective exponent of the coexistence curve toward a larger value is Fisher renormalization from β to $\beta/(1-\alpha)$ caused by impurities [27].

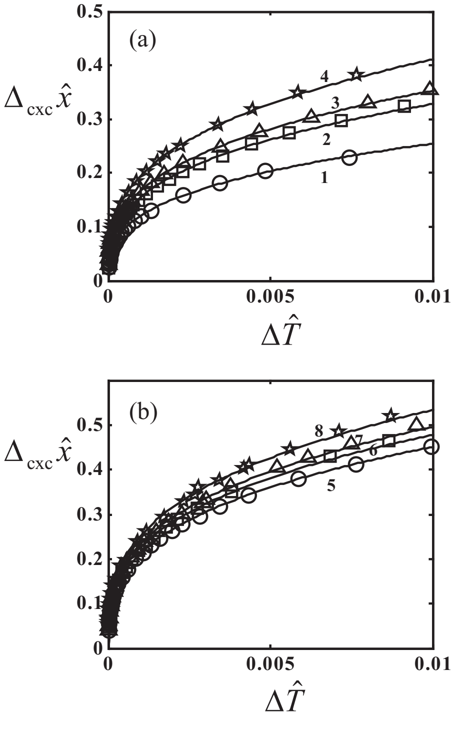

FIG. 1. Mole-fraction difference $\Delta\hat{x}_{cxc}\equiv(x'-x'')/2x_c$ of the liquid-liquid coexistence curves for nitrobenzene+n-pentane (1), n-heptane (2), n-octane (3), n-decane (4), n-undecane (5), n-tridecane (6), n-tetradecane (7), and n-hexadecane (8) as a function of $|\Delta\hat{T}|$. The solid curves represent the asymptotic power law for $\Delta_{cxc}\hat{x}$ given by Eq. (59).

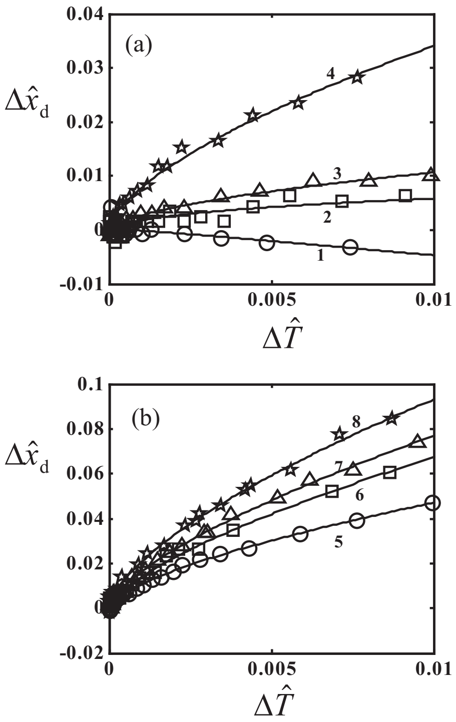

FIG. 2. Diameter $\Delta x_d \equiv (x' + x'')/2x_c - 1$ of the liquid-liquid coexistence curves for nitrobenzene+*n*-pentane (1), *n*-heptane (2), *n*-octane (3), *n*-decane (4), *n*-undecane (5), *n*-tridecane (6), *n*-tetradecane (7), and *n*-hexadecane (8) as a function of $|\Delta\hat{T}|$. The solid curves represent Eq. (61).

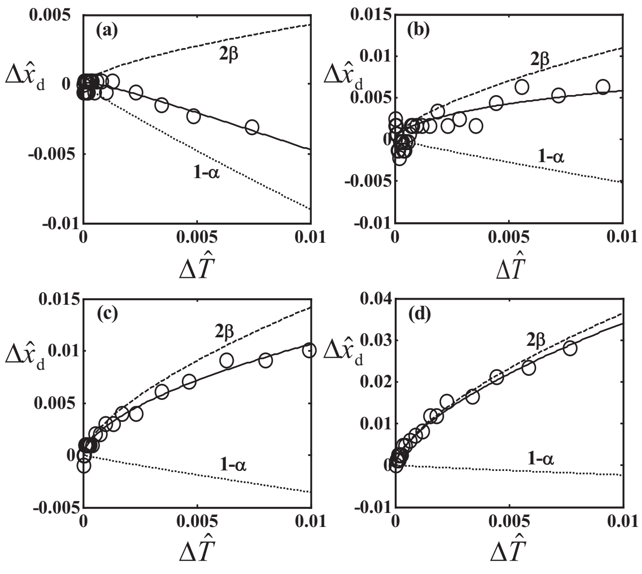

FIG. 3. Diameter $\Delta x_d \equiv (x' + x'')/2x_c - 1$ of the liquid-liquid coexistence curves for nitrobenzene+*n*-pentane (a), +*n*-heptane (b), +*n*-octane (c), +*n*-decane (d) as a function of $|\Delta\hat{T}|$. The symbols indicate experimental data. The solid curves represent Eq. (61), the dashed curve represents the contribution from the 2β term, and the dotted curve the combined contribution from the $1-\alpha$ and linear terms.

The experimental data for the coexistence-curve diameters of the nitrobenzene+*n*-alkane mixtures are shown in Fig. 2 as a function of $|\Delta\hat{T}|$. The diameters of nitrobenzene +*n*-pentane and of nitrobenzene+*n*-heptane exhibit little asymmetry, but the asymmetry becomes more and more pronounced the higher the number of carbon atoms in the alkanes. The solid curves in Fig. 2 represent fits to Eq. (61) with the a_{eff} and b_{eff} as adjustable coefficients. To account for the correlation between the $|\Delta\hat{T}|^{1-\alpha}$ and $|\Delta\hat{T}|$ term in the expansion we have adopted $A_0^- = 5.16$ and $\hat{B}_{\mathrm{cr}} = 2.66$ deduced from experimental data of the two-phase molar heat capacity of nitroethane+isooctane as a typical liquid mixture [6]. There are no experimental data on these values for the nitrobenzene+*n*-alkane mixtures. Therefore, the values obtained for D_1 may be somewhat affected by a system dependence of A_0^- and $\hat{B}_{\mathrm{cr}}$. The values obtained for the asymmetry coefficients, together with the corresponding values of the amplitudes D_2 and D_1 of the contributions proportional to $|\Delta\hat{T}|^{2\beta}$ and $|\Delta\hat{T}|^{1-\alpha}$, respectively, are listed in Table II. The relative contributions of the two sources of asymmetry to the coexistence-curve diameters are shown in Figs. 3 and 4. For nitrobenzene+*n*-pentane and nitrobenzene+*n*-heptane, both contributions are small and, moreover, have opposite signs. With increase of the alkane carbon number the contribution from the $1-\alpha$ singular term becomes smaller and even slightly negative, while the contribution from the 2β singular

TABLE II. Asymmetry parameters for binary liquid mixtures of nitrobenzene with *n*-alkanes; σ is the standard deviation of a fit of Eq. (61) to the experimental data.

System	D_2	D_1	a_{eff}	b_{eff}	10σ
NB+C_5 [34]	0.086	0.073	0.066	0.073	0.01
NB+C_6 [32]	0.180	0.043	0.103	0.053	0.01
NB+C_7 [32]	0.220	0.042	0.102	0.042	0.01
NB+C_8 [33]	0.285	0.029	0.114	0.029	0.01
NB+C_{10} [34]	0.730	0.019	0.216	0.019	0.02
NB+C_{11} [35]	0.978	0.014	0.240	0.014	0.03
NB+C_{12} [36]	0.990	0.024	0.231	0.024	0.06
NB+C_{13} [37]	1.16	−0.080	0.252	−0.080	0.02
NB+C_{14} [38]	1.36	−0.072	0.277	−0.072	0.01
NB+C_{16} [39]	1.85	−0.007	0.324	−0.007	0.02

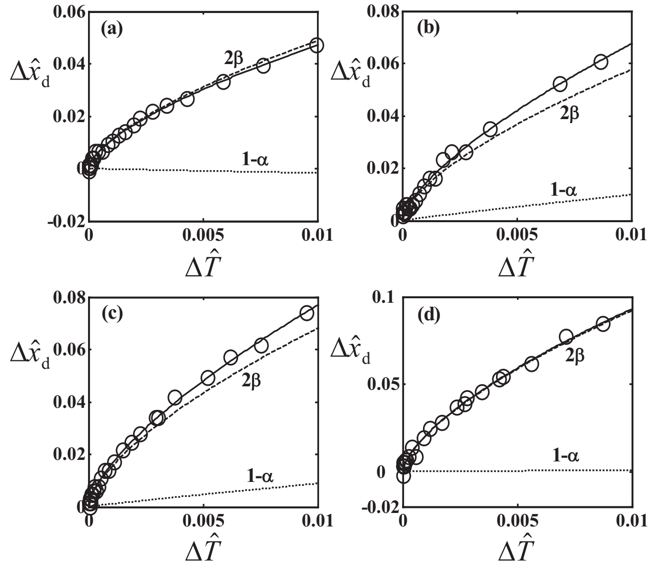

FIG. 4. Diameter $\Delta x_d \equiv (x'+x'')/2x_c - 1$ of the liquid-liquid coexistence curves for nitrobenzene+n-undecane (a), +n-tridecane (b), +n-tetradecane (c), and +n-hexadecane (d) as a function of $|\Delta\hat{T}|$. The symbols indicate experimental data. The solid curves represent Eq. (61), the dashed curve represents the contribution from the 2β term, and the dotted curve the combined contribution from the $1-\alpha$ and linear terms.

term increases significantly and becomes the dominant contribution to the diameter.

We note that $D_2 = a_{\text{eff}} B_0^2$, in accordance with Eq. (54), so that the contribution to the diameter from the 2β singular term is controlled by the coefficient $a_{\text{eff}} = -a_1/x_c(1-x_c a_1)$ resulting from complete scaling. From Eqs. (42) and (43) it follows that in lowest approximation $\Delta\hat{\rho}/\Delta\hat{x} = -a_{\text{eff}}$. Physically, this means that, while the $D_1|\Delta\hat{T}|^{1-\alpha}$ term originates from a correlation between concentration and entropy, the $D_2|\Delta\hat{T}|^{2\beta}$ term originates from a correlation between concentration and density. Estimating

$$\frac{\Delta\hat{\rho}}{\Delta\hat{x}} \approx \frac{x_c}{\rho_c}(\rho_{\text{alk}} - \rho_{\text{NB}}) \simeq k\left(1 - \frac{v_{\text{alk}}}{v_{\text{NB}}}\right), \tag{62}$$

where $x_c/\rho_c v_{\text{alk}}$ is approximated as a constant k, one obtains $D_2/B_0^2 = a_{\text{eff}} \simeq k(v_{\text{alk}}/v_{\text{NB}} - 1)$. Figure 5(a) illustrates that such a rough estimate is in remarkable agreement with experiment. In Fig. 5(b) we also show the asymmetry coefficients b_{eff} as a function of the molecular-volume ratio $v_{\text{alk}}/v_{\text{NB}}$. The coefficient a_{eff} increases linearly with this ratio, while the coefficient b_{eff} decreases with increasing values of $v_{\text{alk}}/v_{\text{NB}}$, although the values of b_{eff} are much smaller and, hence, exhibit much more scatter than the values of a_{eff}. Nevertheless, from Fig. 5, it is evident that the ratio of the molecular volumes of the two liquid components plays a crucial role in the asymmetry of liquid-liquid equilibrium.

VIII. SOME OTHER CONSEQUENCES OF LIQUID-LIQUID ASYMMETRY

In one-component fluids there exists a well-known relationship between the isochoric molar heat capacity in the two-phase region and the temperature derivatives of the saturation pressure P and the saturation chemical potential μ, commonly referred to as the Yang-Yang relation [42]:

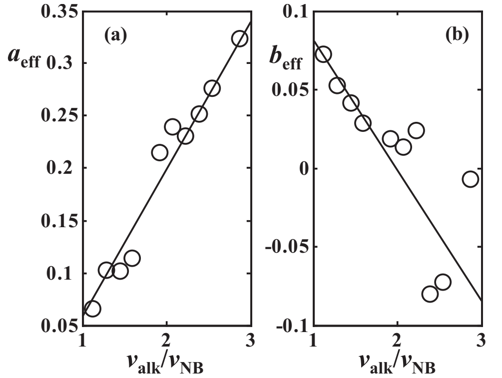

FIG. 5. The asymmetry coefficients a_{eff} and b_{eff} in the scaling fields as a function of $v_{\text{alk}}/v_{\text{NB}}$ for nitrobenzene+n-alkane mixtures.

$$\frac{C_V}{T} = \frac{1}{\rho}\left(\frac{d^2P}{dT^2}\right)_{\text{cxc}} - \left(\frac{d^2\mu}{dT^2}\right)_{\text{cxc}}. \tag{63}$$

Since C_V diverges as $|\Delta\hat{T}|^{-\alpha}$, the question arises whether this divergence is associated with a similar divergence of either $(d^2P/dT^2)_{\text{cxc}}$ or $(d^2\mu/dT^2)_{\text{cxc}}$ or both. In the simple scaling assumption, that is, if one neglects a contribution from the pressure in the definition (9) of the ordering field h_1 only $(d^2P/dT^2)_{\text{cxc}}$ diverges, while $(d^2\mu/dT^2)_{\text{cxc}}$ remains finite. However, as pointed out by Fisher and co-workers [9–11], a significant consequence of complete scaling is that both $(d^2P/dT^2)_{\text{cxc}}$ and $(d^2\mu/dT^2)_{\text{cxc}}$ should diverge. Experimental and computational evidence for such a Yang-Yang anomaly has also been reported by Fisher and co-workers [9–11,43,44].

The analog of Eq. (63) for binary liquid mixtures reads

$$\frac{C_{P,x}}{T} = -\frac{\partial^2}{\partial T^2}(\mu_1 + x\mu_{\Delta 21}) = -x\left(\frac{d^2\mu_{\Delta 21}}{dT^2}\right)_{P,\text{cxc}} - \left(\frac{d^2\mu_1}{dT^2}\right)_{P,\text{cxc}}. \tag{64}$$

Hence, one must expect the presence of a similar Yang-Yang anomaly in binary liquid mixtures. Specifically, it follows from Eq. (35) that at $x = x_c$

$$\left(\frac{d^2\Delta\hat{\mu}_{\Delta 21}}{d\hat{T}^2}\right)_{P,\text{cxc}} = -a_1\left(\frac{d^2\Delta\hat{\mu}_1}{d\hat{T}^2}\right)_{P,\text{cxc}} \simeq a_{\text{eff}}\frac{\hat{C}_P}{\hat{T}} \propto |\Delta\hat{T}|^{-\alpha}. \tag{65}$$

By measuring $C_{P,x}/T$ in the two-phase region at different overall compositions x and plotting the data as a function of x, one can obtain $(d^2\mu_{\Delta 21}/dT^2)_{\text{cxc}}$ from the slope and $-(d^2\mu_1/dT^2)_{\text{cxc}}$ from the intercept at $x=0$, with both values diverging at the critical temperature. In a symmetric binary liquid mixture, $a_1 = 0$ in Eq. (65) and $(d^2\mu_{\Delta 21}/dT^2)_{\text{cxc}}$ should not diverge.

As pointed out by Kim *et al.* [11], for one-component fluids complete scaling also affects the temperature dependence of the susceptibilities χ' and χ'' of the two coexisting phases. For this purpose they considered the ratio

$$A_\chi(T) \equiv \frac{\chi' - \chi''}{\chi' + \chi''}. \qquad (66)$$

For liquid mixtures the corresponding susceptibility is to be identified with the osmotic compressibility $\chi = (\partial x / \partial \mu_{\Delta 21})_{P,T}$. In incomplete scaling with $a_1 = 0$, $A_\chi(T)$ should vanish as $|\Delta\hat{T}|^{1-\alpha-\beta}$, but in complete scaling with $a_1 \neq 0$ it should vanish as $|\Delta\hat{T}|^{\beta}$ [11].

Finally, liquid-liquid asymmetry is also responsible for the curvature correction to the interfacial tension of the two coexisting liquid phases [45], which is defined through $\sigma = \sigma_\infty(1 - 2\delta/R)$, where σ_∞ is the surface tension for the planar interface, $1/R$ is the curvature of the interface, and the coefficient δ is known as Tolman's length. In a one-component fluid Tolman's length can be estimated through a thermodynamic relation [45],

$$\frac{\delta}{2\xi} = \frac{\Delta\hat{\rho}_{\mathrm{d}}}{\hat{\rho}' - \hat{\rho}''}, \qquad (67)$$

where ξ is the half-width of the interface, equal to the correlation length of critical fluctuations [46]. For incompressible binary liquids an equation analogous to Eq. (67) should read

$$\frac{\delta}{2\xi} = \frac{\Delta x_{\mathrm{d}}}{x' - x''}. \qquad (68)$$

The correlation length below the critical point diverges asymptotically as

$$\xi \approx \xi_0 |\Delta\hat{T}|^{-\nu} \qquad (69)$$

with ξ_0 being the amplitude of the correlation length, usually 0.1–0.3 nm. As follows from Eq. (69), Tolman's length diverges at the liquid-liquid critical point as

$$\delta \simeq \mp \xi_0 \left(a_{\mathrm{eff}} B_0 |\Delta\hat{T}|^{\beta-\nu} - b_{\mathrm{eff}} \frac{A_0^-}{1-\alpha} |\Delta\hat{T}|^{1-\alpha-\beta-\nu} \right), \qquad (70)$$

where $\beta - \nu \simeq 0.304$ and $1 - \alpha - \beta - \nu \simeq 0.044$; $\mp$ correspond to a droplet enriched with the solvent or the solute, respectively. The more strongly divergent term, $\sim |\Delta\hat{T}|^{\beta-\nu}$, emerges in complete scaling, while incomplete scaling predicts only a very weak singularity, proportional to $|\Delta\hat{T}|^{1-\alpha-\beta-\nu}$, which is insignificant in practice. In mean-field approximation Tolman's length remains a constant of the order of the molecular size. One obtains for the nitrobenzene+*n*-hexadecane mixture at $\Delta\hat{T} \simeq 10^{-4}$ a mesoscopic Tolman length $|\delta| \simeq 5$ nm by using the values $\xi_0 \simeq 0.2$ nm, $B_0 \simeq 2.4$, $a_{\mathrm{eff}} \simeq 0.32$, and $b_{\mathrm{eff}} \approx 0$, whereas the width of the liquid-liquid interface remains much larger since $\xi \simeq 66$ nm.

IX. DISCUSSION

In this paper we have reformulated the extension of the principle of critical-point universality to binary fluid mixtures in terms of complete scaling, a concept that properly matches asymmetric fluid-phase behavior with the symmetric Ising model. We have clarified the proper definition of the order parameter in binary fluid mixtures. Complete scaling implies that the order parameter is to be defined as a combination of all density-like variables that are conjugate to all (independent and dependent) physical fields. The universal order parameter is symmetric, as in the Ising model, whereas experimentally observed physical densities are asymmetric. We have shown that asymmetry of liquid-liquid coexistence originates from two different sources: one is associated with the correlation between concentration and entropy fluctuations, whereas the other source is the correlation between concentration and density fluctuations. Thus we have found that, even in incompressible binary solutions, there may be a strong asymmetry in liquid-liquid coexistence behavior. This asymmetry in first approximation is controlled by three coefficients in the relation between the theoretical scaling fields, given by Eqs. (39)–(41), namely, a_1, b_2, and b_4. The coefficient b_2 can be obtained experimentally from the asymmetry of the molecular density of the coexisting liquid phases, given by Eq. (42). The coefficient $a_{\mathrm{eff}} = -a_1 / x_{\mathrm{c}}(1 - x_{\mathrm{c}} a_1)$ and a combination $b_{\mathrm{eff}} = (b_4 - x_{\mathrm{c}} b_2) / x_{\mathrm{c}}(1 - \hat{S}_{\mathrm{c}} b_2)$ can be obtained from the near-asymptotic asymmetry in the mole fractions as given by Eq. (43). By taking the difference of the mole fractions for the two coexisting phases, one obtains the property that asymptotically behaves as the order parameter. However, in accordance with Eq. (46), even this symmetric property is affected by nonasymptotic asymmetric terms; the leading correction term, proportional to $\pm a_1^2 B_0^3 |\Delta T|^{3\beta}$, originates from a coupling between the density and concentration fluctuations and depending on the asymmetry coefficient a_1.

By analyzing the coexisting curves of liquid solutions of nitrobenzene in a series of hydrocarbons (from *n*-pentane to *n*-hexadecane), we have separated these two sources of asymmetry and have found that the leading nonanalytical contribution to the asymmetry strongly correlates with the solute-solvent molecular-volume ratio. To separate the contributions from the coefficients b_2 and b_4 one needs independent data on the molecular densities along the liquid-liquid coexistence curve. One should also notice that there is a certain difference in the manner in which the asymmetry coefficients are defined for liquid-liquid equilibria in binary solutions and for vapor-liquid equilibria in one-component fluids, namely, a prefactor $1/x_{\mathrm{c}}$ appears in expressions (55) and (56) for a_{eff} and b_{eff}. This difference originates from the way in which the dependent field h_3 in Eq. (24) is made dimensionless. Upon normalizing h_3 by ρ_{c}, the coefficients c_1 and c_2 become $c_1 = \hat{\rho}_{\mathrm{c}} = 1$ and $c_2 = -\hat{\rho}_{\mathrm{c}} = -1$, while $c_4 = -\hat{\rho}_{\mathrm{c}} x_{\mathrm{c}} = -x_{\mathrm{c}}$. The signs of a_{eff} and b_{eff} depend on the choice of solvent and solute concentration. If nitrobenzene were chosen as the solute, the coefficient a_1 would be positive and thus a_{eff} would be negative.

To explicitly model liquid-liquid asymmetry in nitrobenzene+*n*-alkane solutions, we consider the chemical-potential difference

$$\hat{\mu}_{\Delta 21} = \frac{\partial}{\partial x}(\hat{\mu}_1 + x\hat{\mu}_{\Delta 21}) \qquad (71)$$

in the form [12]

$$\hat{\mu}_{\Delta 21} - \hat{\mu}^{0}_{\Delta 21} = \left(\frac{\hat{T}}{N}\ln \phi - \hat{T}\ln(1-\phi)\right) - 2\omega_0\phi\left(1 - \frac{3}{4}\omega_1\phi\right), \tag{72}$$

where $N = v_{\text{alk}}/v_{\text{NB}}$ is the ratio of the solute-solvent molecular volumes, ω_0 and ω_1 are interaction constants, and ϕ is a normalized mole fraction. When $N=1$ and $\omega_1=0$, Eq. (72) reduces to the symmetric "regular-solution" model, equivalent to a symmetric binary lattice with $\phi_c=0.5$.

Formally, Eq. (72) is equivalent to the Flory-Huggins model [47,48] for describing thermodynamics of long polymer chains with $N \gg 1$ and with ϕ being the polymer volume fraction. However, we regard Eq. (72) as a mean-field model with N being a phenomenological parameter which is allowed to be any number, even fractional, and ϕ the mole fraction normalized as $\phi/x = 0.5/x_{c,N=1}$ such that $\phi_c=0.5$ when $N=1$ and $\omega_1=0$.

The relations between the scaling fields are assumed to be unaffected by the critical fluctuations. However, in the critical region the fluctuations renormalize the temperature dependences of ϕ_1 and ϕ_2, as well as the coupling between the concentration, density, and entropy, and thus make the fluid-phase asymmetry nonanalytic. Therefore, one can obtain the asymmetry coefficients a_{eff} and b_{eff} directly from a mean-field equation of state. Using the method developed in Ref. [12], one can show that the asymmetry coefficient a_{eff} for the model given by Eq. (72) can be expressed through the mean-field derivatives of the chemical-potential difference $\mu_{\Delta 21}$ as

$$a_{\text{eff}} = \frac{2}{3}\frac{\partial^3 \mu_{\Delta 21}/\partial \phi^2\, \partial T}{\partial^2 \mu_{\Delta 21}/\partial \phi\, \partial T} - \frac{1}{5}\frac{\partial^4 \mu_{\Delta 21}/\partial \phi^4}{\partial^3 \mu_{\Delta 21}/\partial \phi^3}. \tag{73}$$

In Fig. 6 the asymmetry coefficients a_{eff}, calculated with Eq. (73) from the model given in Eq. (72), are compared with their experimental values. Since the values of $N = v_{\text{alk}}/v_{\text{NB}}$ and x_c are known, the only parameter to be adjusted is the three-body interaction parameter ω_1. As seen from Fig. 6, this rather primitive model reasonably describes the behavior of a_{eff} for the nitrobenzene+n-alkane solutions with the three-body interaction parameter ω_1 changing from 1 to zero.

Due to a lack of experimental data on the isobaric heat capacity for the nitrobenzene+n-alkane mixtures, for fitting the data to Eq. (61) we had to approximate the amplitudes A_0^- and B_{cr} as constant values obtained for a similar mixture of nitroethane+isooctane [6]. Independent experiments on the isobaric heat capacities for binary liquid solutions with different solute-solvent molecular-volume ratios would enable one not only to more accurately determine the coefficient b_{eff}, but also to verify the analog of the Yang-Yang anomaly for binary liquid mixtures given by Eq. (65).

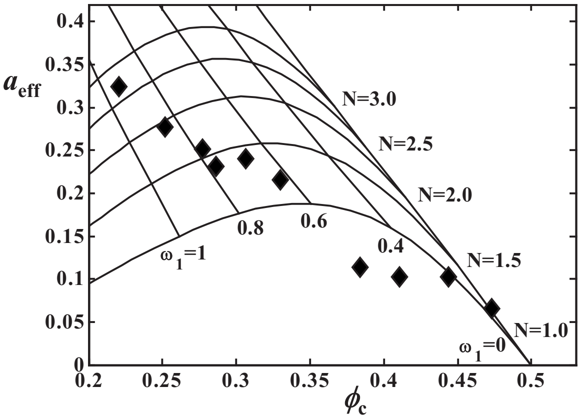

FIG. 6. Parameter a_{eff} calculated with Eq. (73) from the model given by Eq. (72). Solid diamonds indicate a_{eff} for nitrobenzene +n-alkane mixtures.

Finally, the predicted thermodynamic relation between the Tolman length and the asymmetry in liquid-liquid phase equilibria given by Eq. (68), as well as the divergence of the Tolman length at the critical point, make accurate experiments and simulations on the curvature dependence of the interfacial tension highly desirable.

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