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# Dielectric constant of fluids and fluid mixtures at criticality

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The behavior of the dielectric constant $\varepsilon$ of pure fluids and binary mixtures near liquid-gas and liquid-liquid critical points is studied within the concept of complete scaling of asymmetric fluid-fluid criticality. While mixing of the electric field into the scaling fields plays a role, pressure mixing is crucial as the asymptotic behavior of the coexistence-curve diameter in the $\varepsilon$—$T$ plane is concerned. Specifically, it is found that the diameters, characterized by a $|T-T_c|^{1-\alpha}$ singularity in the previous scaling formulation [J. V. Sengers, D. Bedeaux, P. Mazur, and S. C. Greer, Physica A **104**, 573 (1980)], gain a more dominant $|T-T_c|^{2\beta}$ term, whose existence is shown to be supported by literature experimental data. The widely known $|T-T_c|^{1-\alpha}$ singularity of $\varepsilon$ along the critical isopleth in the one-phase region is found to provide information on the effect of electric fields on the liquid-liquid critical temperature: from experimental data it is inferred that $T_c$ usually decreases as the magnitude of the electric field is enhanced. Furthermore, the behavior of mixtures along an isothermal path of approach to criticality is also analyzed: theory explains why the observed anomalies are remarkably higher than those associated to the usual isobaric path.

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## I. INTRODUCTION

Despite the story of critical behavior of the dielectric constant $\varepsilon$ of fluid systems started in 1932 [1], substantial progress was achieved in the 1970s after the establishment of the modern theory of critical phenomena. All that led to the current *scaling* description of $\varepsilon$ [2], due to Sengers, Bedeaux, Mazur, and Greer (SBMG), which dates to 1980. Since then, a number of experimental findings as well as newly developed conceptual issues make this topic to deserve further attention.

For both pure fluids and mixtures in the two-phase region, SBMG predicts that the coexistence-curve diameter $\varepsilon_d(T)$, namely, the midpoints of the phase boundary in the $\varepsilon-T$ plane, behaves like [3]

$$\varepsilon_d(T) \equiv \frac{\varepsilon^+(T)+\varepsilon^-(T)}{2} = \varepsilon_c + E_{1-\alpha}|t|^{1-\alpha} + E_1|t| + \cdots, \tag{1.1}$$

where $t \equiv (T-T_c)/T_c$, $\alpha \simeq 0.109$ [4], while + and − refer to the coexisting phases. From an experimental point of view, little attention has been paid to this subject for pure fluids, while results for liquid-liquid phase transitions have evidenced that $\varepsilon_d(T)$ can have a significant curvature: specifically, as noted in 1988 by Kindt *et al.* [5] and Tveekrem *et al.* [6], data on mixtures point toward the existence of a $|t|^{2\beta}$ (with $\beta \simeq 0.326$ [4]) contribution, which dominates the $|t|^{1-\alpha}$ one in Eq. (1.1) since $2\beta < 1-\alpha$. From a theoretical perspective, Goulon *et al.* [7] encountered that the coexistence-curve diameter of a droplet model for consolute critical phenomena in binary mixtures displays a $|t|^{2\beta}$ contribution. Such an inconsistency between results from the droplet model and those steaming from scaling was originally noted in SBMG.

How could then the $|t|^{2\beta}$ singularity be accommodated into scaling theory? In 2000, the scaling description of critical phenomena in fluids was revised by Fisher and coworkers [8–11] in connection with the so-called Yang-Yang anomaly. The generalization of this novel formulation, termed *complete scaling*, to binary-fluid criticality is straightforward [12–15]. In this context, it is natural to expect that the extension of SBMG within the idea of complete scaling might eventually resolve the above-described discrepancies in the two-phase region. As will be shown, this is actually the case.

When the critical point is approached in the one-phase region, either along the critical isochore of pure fluids or along the critical isopleth (at constant pressure) of binary liquid-liquid systems, SBMG predicts that

$$\varepsilon(T) = \varepsilon_c + \bar{E}_{1-\alpha}|t|^{1-\alpha} + \bar{E}_1|t| + \cdots. \tag{1.2}$$

These $|t|^{1-\alpha}$ anomalies find experimental support from measurements for CO [16] and for a quite large number of binary mixtures (see, among others, Refs. [17–30]). For the latter, it was found [2] that

$$\bar{E}^m_{1-\alpha} = \mp\left[\left(\frac{\partial \breve{T}_c}{\partial \breve{E}'}\right)_p + \varepsilon_c\left(\frac{\partial \breve{T}_c}{\partial \breve{p}}\right)_{E'}\right]\frac{A^+_m}{1-\alpha}, \tag{1.3}$$

where − and + apply to upper (UCP) and lower (LCP) consolute points, respectively, $E' \equiv \varepsilon_0 E^2/2$, while $A^+_m$, $(\partial \breve{T}_c/\partial \breve{E}')_p$, and $(\partial \breve{T}_c/\partial \breve{p})_{E'}$ denote the critical amplitude of the dimensionless isobaric heat capacity and the dimensionless slopes of the critical surface in planes of constant pressure and electric field. (Precise definition of these quantities will be provided later.)

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Clearly, Eqs. (1.2) and (1.3), which remain valid in complete scaling, may provide useful information on $(\partial \breve{T}_c / \partial \breve{E}')_p$. On thermodynamic grounds, $(\partial \breve{T}_c / \partial \breve{E}')_p$ is, by analogy with $(\partial \breve{T}_c / \partial \breve{p})_{E'}$, expected to be unrestricted in sign and magnitude. Experiments [31–34] and theoretical developments by Onuki [35] revealed contradictory results (see, e.g., Ref. [36]). Hence, indirect evaluation of $(\partial \breve{T}_c / \partial \breve{E}')_p$ via $\varepsilon$ studies may be regarded as a promising alternative. We are therefore led to accomplish such a task, which gains importance on recalling recent studies on the role of electric fields in phase equilibria of solutions [36–39].

In addition to analyses as a function of temperature, significant experimental work along the experimentally seldom studied isothermal path has appeared in the last years (see Refs. [40–44]). The following equations were employed for data treatment [45]:

$$\varepsilon_d(p) \equiv \frac{\varepsilon^+(p) + \varepsilon^-(p)}{2} = \varepsilon_c + E^m_{1-\alpha^*}|\hat{p}|^{1-\alpha} + E^m_{1^*}|\hat{p}| + \cdots , \tag{1.4}$$

$$\varepsilon(p) = \varepsilon_c + \bar{E}^m_{1-\alpha^*}|\hat{p}|^{1-\alpha} + E^m_{1^*}|\hat{p}| + \cdots , \tag{1.5}$$

the latter being referred to the critical isopleth in the one-phase region. Clearly, these expressions must be revised according to complete scaling. Furthermore, as noted originally, studies as a function of pressure exhibit remarkable features that claim for reanalysis: the main question to be addressed is to determine and characterize the relation between $E^m_{1-\alpha^*}$ and $E^m_{1-\alpha}$, etc.

In the light of this background, we present here a detailed study on the critical behavior of $\varepsilon$ from both theoretical and experimental standpoints. Theoretically, we consider, as a starting point, the system in the presence on an external electric field that is assumed to leave the (Ising-like) universality class unchanged. This idea is introduced after Sec. II, where basic concepts are reviewed. Then, in Secs. III and IV, we derive, in the framework of complete scaling, expressions of $\varepsilon$ that supplement Eqs. (1.1)–(1.5) above. In Sec. V, selected, reliable experimental data, mostly appeared after 1980, are analyzed and discussed: for the two-phase region, we concentrate on the predicted $|t|^{2\beta}$ terms for the $\varepsilon_d(T)$ of pure fluids and mixtures as well as on the $|\hat{p}|^{2\beta}$ one for the $\varepsilon_d(p)$ of mixtures; for the one-phase region, attention is focused on the behavior of $(\partial \breve{T}_c / \partial \breve{E}')_p$ as inferred from the values of the critical amplitude of the $|t|^{1-\alpha}$ singularity. Section VI contains a summary of results and some recommendations for future experimental work.

## II. BACKGROUND INFORMATION

Here, we will outline some basic, relevant theoretical issues [46]. After introducing scaling, the idea of field mixing in fluid-fluid (i.e., liquid-gas, liquid-liquid, and gas-gas) is described and the concept of nonordering field is explained. We then provide an account of the thermodynamics of fluids and fluid mixtures under an electric field.

### A. Scaling: Fundamentals

According to renormalization-group principles, near a critical point there is a field-dependent thermodynamic potential $\Pi$ that splits up into two pieces: background (or regular) and singular (or critical)

$$\Pi = \Pi^{\text{bg}} + \Pi^{\text{sing}}, \tag{2.1}$$

where $\Pi^{\text{sing}}$ represents the relevant part of the problem, while $\Pi^{\text{bg}}$ is an analytic contribution that is always required. The singular part depends on two *relevant* scaling fields, $\tilde{h}$ (ordering) and $\tilde{t}$ (thermal), say

$$d\Pi^{\text{sing}} = \tilde{m}d\tilde{h} + \tilde{s}d\tilde{t}, \tag{2.2}$$

where the first-order derivatives $\tilde{m}$ and $\tilde{s}$ are the scaling (strong and weak) densities [47]. (For convenience, hereafter, the thermodynamic potential, the scaling fields, and the scaling densities will be made dimensionless.) It is important to point out that we have not considered *irrelevant* scaling fields, which produce correction-to-scaling terms (the reader may consult Ref. [9] for a full account of the various effects of such scaling fields).

Scaling asserts that asymptotically close to criticality

$$\Pi^{\text{sing}} \approx Q|\tilde{t}|^{2-\alpha}W_{\pm}(y), \tag{2.3}$$

where $W_{\pm}$ is the scaling function (with + and − applying to $\tilde{t}>0$ and $\tilde{t}<0$, which define the one-phase region and coexistence, respectively), $y=U\tilde{h}/|\tilde{t}|^{2-\alpha-\beta}$ is the scaling variable, and $Q$ and $U$ are nonuniversal, positive constants; the critical exponents $\alpha$ and $\beta$ take on the universal values specified in Sec. I, which are characteristic of the universality class of the three-dimensional Ising model. The exact functional form of $W_{\pm}$ is not known, but only some conditions it must fulfill (e.g., symmetry requirements, etc.). Accordingly, for small $y$ values, the following expansions apply [48]:

$$W_+ = W_{+0} + W_{+2}y^2 + \cdots , \tag{2.4}$$

$$W_- = W_{-0} + W_{-1}|y| + W_{-2}y^2 + \cdots , \tag{2.5}$$

where, by choosing appropriate values for $Q$ and $U$ and using the accepted values for the universal ratios between critical amplitudes, we can adopt $W_{+0}=W_{+2}=1$, $W_{-0}\simeq 1.9$, and $W_{-1}\sim 2.4$, while $W_{-2}$ is positive as required by thermodynamic convexity [49]. Expressions for $W_{\pm}$ when $y$ is large can be found elsewhere [48]. (They are not shown since no use of them will be made in this work.)

The scaling densities are easily obtained from Eqs. (2.3)–(2.5)

$$\tilde{m} = \left(\frac{\partial \Pi^{\text{sing}}}{\partial \tilde{h}}\right)_{\tilde{t}} = \begin{cases} 2QUW_{+2}|\tilde{t}|^{\beta}y + \cdots & \text{for } \tilde{t} > 0 \\ QU|\tilde{t}|^{\beta}[\sigma_{\tilde{h}}W_{-1} + 2W_{-2}y + \cdots] & \text{for } \tilde{t} < 0, \end{cases} \tag{2.6}$$

$$\tilde{s} = \left(\frac{\partial \Pi^{\mathrm{sing}}}{\partial \tilde{t}}\right)_{\tilde{h}} = \begin{cases} (2-\alpha)QW_{+0}|\tilde{t}|^{1-\alpha}+\cdots & \text{for } \tilde{t}>0 \\ -Q|\tilde{t}|^{1-\alpha}[(2-\alpha)W_{-0}+\sigma_{\tilde{h}}\beta W_{-1}y+\cdots] & \text{for } \tilde{t}<0, \end{cases} \tag{2.7}$$

where $\sigma_{\tilde{h}}=\mathrm{sgn}(\tilde{h})$ is a signum factor. The behavior of second-order derivatives (or susceptibilities) can be straightforwardly obtained (any interested reader can consult, for instance, Refs. [50,51]).

### B. Field mixing and the role of nonordering fields

For a symmetric system such as a uniaxial ferromagnet $\tilde{h}$ and $\tilde{t}$ are, to leading order, identified to physical fields: hence, $\tilde{h} \approx H$ and $\tilde{t} \approx t$ and, consequently, $\Pi$ is the (dimensionless) free energy per spin $\hat{f}=-F/Nk_BT_c$ (where $k_B$ denotes the Boltzmann constant). In the case of (asymmetric) fluid-fluid criticality, it is widely accepted that the scaling fields are, in general, algebraic combinations of the physical fields. This feature is termed *field mixing*. Since the specific relation between scaling fields and physical fields is not known *a priori*, it is a central task to accurately characterize it; such a problem has been usually approached from experiments and statistical mechanical models.

The above description is restricted to an isolated critical point in the phase diagram. In many cases, there is an extra field variable that *merely* develops a line of critical points or *lambda* line. In other words, the presence of such a variable, often referred to as a *nonordering field* [52], does not change the universality class of the phase transition. One of the most typical examples is that of liquid-liquid demixing in binary mixtures, where pressure is a nonordering field.

Scaling in the "presence" of nonordering fields has been studied in SBMG as well in other contexts, including behavior near critical end points [48,52]. Furthermore, the role of pressure as a nonordering field in connection with complete scaling for the case of liquid-liquid demixing in *weakly* compressible binary mixtures has been characterized [15].

### C. Thermodynamics of systems under an electric field

We shall be concerned with a system in the presence of an external electric field; since we will be dealing with isotropic systems, only its magnitude $E$ matters. The thermodynamics can be written as [2]

$$dU = TdS - pdV + \mu dN + Ed(DV), \tag{2.8}$$

where $D$ denotes the electric displacement while the remaining variables have their usual meaning. The Gibbs-Duhem equation is

$$-SdT + Vdp - Nd\mu - DVdE = 0. \tag{2.9}$$

On dividing by $V$, one gets

$$dp = \rho SdT + \rho d\mu + DdE, \tag{2.10}$$

where $\rho S$ and $\rho$ denote the entropy density and the number density, respectively. In turn, $D$ is related to $E$ via

$$D = \varepsilon_0 \varepsilon E, \tag{2.11}$$

where $\varepsilon_0$ and $\varepsilon$ denote the vacuum permittivity and the dielectric constant, respectively. By combining Eqs. (2.10) and (2.11) we get

$$dp = \rho SdT + \rho d\mu + \varepsilon dE', \tag{2.12}$$

where, recall, $E' \equiv \varepsilon_0 E^2/2$. It is important to point out that despite $D$ (density) and $E$ (field) are the basic pair of variables characterizing the electrostatic part of the problem, it will prove very useful to consider $\varepsilon$ and $E'$ as Eq. (2.12) dictates. In terms of dimensionless critical deviations, we have

$$d\hat{p} = \hat{\rho}\hat{S}dt + \hat{\rho}d\hat{\mu} + \varepsilon d\hat{E}', \tag{2.13}$$

where

$$\hat{p} \equiv (p-p_c)/\rho_c k_B T_c, \quad \hat{\mu} \equiv (\mu-\mu_c)/k_B T_c,$$

$$\hat{E}' \equiv (E'-E'_c)/\rho_c k_B T_c \tag{2.14}$$

and

$$\hat{\rho}\hat{S} \equiv \frac{\rho S}{\rho_c k_B}, \quad \hat{\rho} \equiv \frac{\rho}{\rho_c}. \tag{2.15}$$

For binary mixtures, we start from

$$dU = TdS - pdV + \mu_1 dN_1 + \mu_2 dN_2 + Ed(DV). \tag{2.16}$$

The Gibbs-Duhem equation can be expressed as

$$-SdT + Vdp - Nd\mu_1 - N_2 d\mu_{21} - V\varepsilon dE' = 0, \tag{2.17}$$

where $\mu_{21} \equiv \mu_2 - \mu_1$. Here, it is convenient to divide by $N$ to get

$$d\mu_1 = -sdT + vdp - x_2 d\mu_{21} - v\varepsilon dE', \tag{2.18}$$

where $s$, $v$, and $x_2$ denote the entropy per particle, the volume per particle, and the mole fraction of component 2, respectively. In terms of dimensionless critical deviations, Eq. (2.18) turns into

$$d\hat{\mu}_1 = -\hat{s}dt + \hat{v}d\hat{p} - x_2 d\hat{\mu}_{21} - \hat{v}\varepsilon d\hat{E}', \tag{2.19}$$

where

$$\hat{\mu}_1 \equiv (\mu_1 - \mu_{1,c})/k_B T_c, \quad \hat{\mu}_{21} \equiv (\mu_{21} - \mu_{21,c})/k_B T_c \tag{2.20}$$

and

$$\hat{s} \equiv \frac{s}{k_B}, \quad \hat{v} \equiv \frac{\mathrm{v}}{\mathrm{v}_c}. \tag{2.21}$$

## III. THEORY FOR PURE FLUIDS

### A. Formulation and general expressions

Complete scaling invokes three relevant scaling fields, $\tilde{h}$, $\tilde{t}$, and $\tilde{g}$, which, to linear order, are combinations of *all* physical fields. For the case of pure-fluid criticality, we have [8–11]

$$\tilde{h} \approx \hat{\mu} - k_1 t - j_2 \hat{p}, \tag{3.1}$$

$$\tilde{t} \approx t - l_1 \hat{\mu} - j_1 \hat{p}, \tag{3.2}$$

$$\tilde{g} \approx \hat{p} - l_0 \hat{\mu} - k_0 t, \tag{3.3}$$

where, without loss of generality, coefficients for the first terms in the right-hand side have been fixed to unity. By choosing $y = U\tilde{h}/|\tilde{t}|^{2-\alpha-\beta}$ as the scaling variable, we may write

$$\tilde{g} \approx Q|\tilde{t}|^{2-\alpha} W_{\pm}(y), \tag{3.4}$$

which replaces Eq. (2.3). [Equations (2.6) and (2.7) change correspondingly.] This clearly implies that $\tilde{g} = \tilde{g}(\tilde{h}, \tilde{t})$ is the singular part of the thermodynamic potential (i.e., $\tilde{g} \equiv \Pi^{\text{sing}}$), which in view of Eq. (3.3) can be $p$, $\mu$, or $T$: by solving such equation for any of them, the remaining two terms in the right-hand side serve to represent the background contribution.

Now we consider the system in the presence of an external electric field of magnitude $E$. We assume that the universality class of the phase transition remains unaltered under such conditions, i.e., $E$ acts as a nonordering field that develops a line of critical points. Consequently [15], the effect of the electric field is expressed by making all nonuniversal parameters in Eqs. (3.1)–(3.3) dependent on $E$, namely,

$$\tilde{h} \approx \hat{\mu}(E) - k_1(E) t(E) - j_2(E) \hat{p}(E), \tag{3.5}$$

$$\tilde{t} \approx t(E) - l_1(E) \hat{\mu}(E) - j_1(E) \hat{p}(E), \tag{3.6}$$

$$\tilde{g} \approx \hat{p}(E) - l_0(E) \hat{\mu}(E) - k_0(E) t(E). \tag{3.7}$$

By expanding Eqs. (3.5)–(3.7) around a given point under investigation on the lambda line, one finds

$$\tilde{h} \approx \hat{\mu} - k_1 t - j_2 \hat{p} - q_2 \hat{E}, \tag{3.8}$$

$$\tilde{t} \approx t - l_1 \hat{\mu} - j_1 \hat{p} - q_1 \hat{E}, \tag{3.9}$$

$$\tilde{g} \approx \hat{p} - l_0 \hat{\mu} - k_0 t - q_0 \hat{E}, \tag{3.10}$$

where $\hat{E} \equiv \varepsilon_0 (E - E_c)/\rho_c^{2/3}$, while

$$q_2 = \left( \frac{\rho_c^{2/3}}{k_B T_c \varepsilon_0} \frac{d\mu_c}{dE} - j_2 \frac{1}{k_B T_c \varepsilon_0 \rho_c^{1/3}} \frac{dp_c}{dE} - k_1 \frac{\rho_c^{2/3}}{T_c \varepsilon_0} \frac{dT_c}{dE} \right), \tag{3.11}$$

$$q_1 = \left( \frac{\rho_c^{2/3}}{T_c \varepsilon_0} \frac{dT_c}{dE} - j_1 \frac{1}{k_B T_c \varepsilon_0 \rho_c^{1/3}} \frac{dp_c}{dE} - l_1 \frac{\rho_c^{2/3}}{k_B T_c \varepsilon_0} \frac{d\mu_c}{dE} \right), \tag{3.12}$$

$$q_0 = \left( \frac{1}{k_B T_c \varepsilon_0 \rho_c^{1/3}} \frac{dp_c}{dE} - k_0 \frac{\rho_c^{2/3}}{T_c \varepsilon_0} \frac{dT_c}{dE} - l_0 \frac{\rho_c^{2/3}}{k_B T_c \varepsilon_0} \frac{d\mu_c}{dE} \right). \tag{3.13}$$

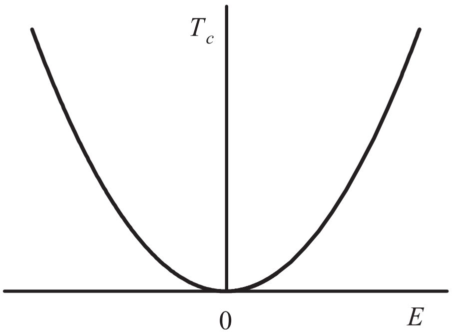

FIG. 1. Schematic representation of the liquid-gas critical line of a pure fluid under an external electric field.

Let us now define the lambda line. To this end, we impose $\tilde{h} = \tilde{t} = \tilde{g} = 0$ in Eqs. (3.8)–(3.10) and solve for $t$ to get

$$t = \Lambda \hat{E} + \cdots, \tag{3.14}$$

from which it follows that

$$\frac{d\breve{T}_c}{d\breve{E}} \equiv \frac{\rho_c^{2/3}}{\varepsilon_0 T_c} \frac{dT_c}{dE} = -\frac{E_p}{T_p}, \tag{3.15}$$

where

$$T_p = 1 - l_1 k_1 - (j_1 + j_2 l_1) \frac{k_0 + k_1 l_0}{1 - j_2 l_0}, \tag{3.16}$$

$$E_p = -\frac{(l_0 q_2 + q_0)(l_1 j_2 + j_1)}{1 - j_2 l_0} - (l_1 q_2 + q_1). \tag{3.17}$$

We shall restrict our analysis to $E=0$, which is a special point on the critical line. Indeed, because of obvious symmetry upon electric field reversal, $dT_c/dE=0$ (see Fig. 1) but also $dp_c/dE = d\mu_c/dE = 0$, implying that $q_2 = q_1 = q_0 = 0$ [see Eqs. (3.11)–(3.13)]. Therefore, in order to express the effect of the electric field, quadratic terms in $E$ must be included in the expansions of the scaling fields. We are then led to consider $E'$, for which, as we have seen in Sec. II C, $\varepsilon$ is the conjugated density. Accordingly,

$$\tilde{h} \approx \hat{\mu}(E') - k_1(E') t(E') - j_2(E') \hat{p}(E'), \tag{3.18}$$

$$\tilde{t} \approx t(E') - l_1(E') \hat{\mu}(E') - j_1(E') \hat{p}(E'), \tag{3.19}$$

$$\tilde{g} \approx \hat{p}(E') - l_0(E') \hat{\mu}(E') - k_0(E') t(E'), \tag{3.20}$$

which yield

$$\tilde{h} \approx \hat{\mu} - k_1 t - j_2 \hat{p} - q_2' \hat{E}', \tag{3.21}$$

$$\tilde{t} \approx t - l_1 \hat{\mu} - j_1 \hat{p} - q_1' \hat{E}', \tag{3.22}$$

$$\tilde{g} \approx \hat{p} - l_0 \hat{\mu} - k_0 t - q_0' \hat{E}', \tag{3.23}$$

where

$$q_2' = \left[ \rho_c \frac{d\mu_c}{dE'} - j_2 \frac{dp_c}{dE'} - k_1 k_B \rho_c \frac{dT_c}{dE'} \right], \tag{3.24}$$

$$q_1' = \left[ k_B \rho_c \frac{dT_c}{dE'} - j_1 \frac{dp_c}{dE'} - l_1 \rho_c \frac{d\mu_c}{dE'} \right], \tag{3.25}$$

$$q_0' = \left[ \frac{dp_c}{dE'} - k_0 k_B \rho_c \frac{dT_c}{dE'} - l_0 \rho_c \frac{d\mu_c}{dE'} \right], \tag{3.26}$$

with

$$\frac{d\breve{T}_c}{d\breve{E}'} \equiv k_B \rho_c \frac{dT_c}{dE'} = - \frac{E_p'}{T_p'}, \tag{3.27}$$

where

$$E_p' = - \frac{(l_0 q_2' + q_0')(l_1 j_2 - j_1)}{1 - j_2 l_0} - (l_1 q_2' + q_1'). \tag{3.28}$$

Thus, we observe that the electric-field-mixing coefficients originate from the dependence of the critical coordinates on $E'$.

To get concrete expressions for the physical densities, let us consider the differential relation

$$d\tilde{g} = \tilde{m} d\tilde{h} + \tilde{s} d\tilde{t}. \tag{3.29}$$

By introducing Eqs. (3.21)–(3.23) into Eq. (3.29) and comparing to Eq. (2.13), one obtains

$$\hat{\rho}\hat{S} = \frac{k_0 - k_1 \tilde{m} + \tilde{s}}{1 + j_2 \tilde{m} + j_1 \tilde{s}}, \tag{3.30}$$

$$\hat{\rho} = \frac{l_0 + \tilde{m} - l_1 \tilde{s}}{1 + j_2 \tilde{m} + j_1 \tilde{s}}, \tag{3.31}$$

$$\varepsilon = \frac{q_0' - q_2' \tilde{m} - q_1' \tilde{s}}{1 + j_2 \tilde{m} + j_1 \tilde{s}}. \tag{3.32}$$

Finally, we note that the SBMG formulation is recaptured from the present one by eliminating the pressure-mixing terms in Eqs. (3.21)–(3.23). As a result, $\tilde{g}$ serves to represent the background part of the "proper" thermodynamic potential, which, in the absence of pressure mixing, is the pressure (see Refs. [2,53,54]).

### B. Two-phase region

In the absence of odd correction to scaling terms, this path of approach to the critical point, to be labeled as "$\sigma$," is defined by $\tilde{h}_\sigma = 0$ (or, equivalently, $y_\sigma = 0$) [9]. Since we will be focused on the behavior at constant electric field, $\hat{E}' = 0$ in Eqs. (3.21)–(3.23). With the aid of Eqs. (3.4) and (2.5), those equations can be solved for $\tilde{t}$ to get to leading order

$$\tilde{t}_\sigma \approx T_p t, \tag{3.33}$$

where the mixing factor $T_p$, defined in Eq. (3.16), is positive.

By introducing Eq. (3.33) in Eqs. (2.6) and (2.7) (for $\tilde{t} < 0$), we obtain

$$\tilde{m}_\sigma \approx \pm QUW_{-1} |T_p|^\beta |t|^\beta, \tag{3.34}$$

$$\tilde{s}_\sigma \approx -(2-\alpha) QW_{-0} |T_p|^{1-\alpha} |t|^{1-\alpha}. \tag{3.35}$$

On substituting these into Eq. (3.32) and expanding the denominator, we get

$$\varepsilon^\pm(T) = \varepsilon_c \pm B_\varepsilon |t|^\beta (1 + e_\theta |t|^\theta + \cdots) + E_{2\beta} |t|^{2\beta} + E_{1-\alpha} |t|^{1-\alpha} + E_1 |t| + \cdots, \tag{3.36}$$

with

$$B_\varepsilon = -[q_2' + \varepsilon_c j_2] QUW_{-1} |T_p|^\beta, \tag{3.37}$$

$$E_{2\beta} = \frac{j_2 (B_\varepsilon)^2}{(q_2' + \varepsilon_c j_2)}, \tag{3.38}$$

$$E_{1-\alpha} = [\varepsilon_c j_1 + q_1'] \frac{A^-}{1-\alpha} |T_p|^{-1}, \tag{3.39}$$

where + and − read for liquid and vapor, respectively. Implicit in the above equations is that $q_0' = \varepsilon_c$, while expressions for $\rho^\pm$ and $(\rho S)^\pm$ yield $l_0 = \hat{\rho}_c \equiv 1$ and $k_0 = \hat{\rho}_c \hat{S}_c$ [9]. In the expansion (3.36), only the first correction to scaling term $|t|^{\beta+\theta}$ (with $\theta \simeq 0.52$ [4]) was included. The linear contribution arises from quadratic terms in Eqs. (3.21)–(3.23), which, for simplicity, are not shown. However, we have decided to explicitly include such background contribution since experimental data suggest [10,11] that it must be considered for a good thermodynamic description. In Eq. (3.39), $A^-$ reads for the critical amplitude of the dimensionless isochoric heat capacity per particle at constant electric field $\hat{C}_{V,E'} \equiv T(\partial S / \partial T)_{V,E'} / N k_B$ in the two-phase region, which can be obtained using the Yang-Yang relation [55] to get (see Ref. [51] for details)

$$A^- = (2-\alpha)(1-\alpha) QW_{-0} |T_p|^{2-\alpha}. \tag{3.40}$$

From Eq. (3.36), the $\varepsilon - T$ diameter is

$$\varepsilon_d(T) = \varepsilon_c + E_{2\beta} |t|^{2\beta} + E_{1-\alpha} |t|^{1-\alpha} + E_1 |t| + \cdots, \tag{3.41}$$

implying that a leading $|t|^{2\beta}$ singularity, which is absent in SMBG since $j_1 = j_2 = 0$, naturally emerges from the scaling formulation developed here. Though other parameters enter at play, the $|t|^{2\beta}$ term exists whenever pressure mixes in the scaling fields [cf. Eqs. (3.38)]. In this context, it is important to recall that pressure mixing was introduced with a view to accommodate the so-called Yang-Yang anomaly; that resulted in other, related singularities, the most remarkable of which being the $|t|^{2\beta}$ contribution to the $\rho - T$ coexistence-curve diameter [8,9]. Therefore, the search of the $|t|^{2\beta}$ term for available experimental $\varepsilon_d(T)$ data has important implications. That point will be examined in Sec. V.

### C. Critical isochore in the one-phase region

To specify this path, hereafter to be labeled as "ci," one must start from Eq. (3.31). By introducing the results (2.6) and (2.7) (for $\tilde{t} > 0$) and using Eq. (2.4)—$y$ is small along this path—one gets (see Ref. [9] for more details)

$$y = Y_1 |\tilde{t}|^{1-\alpha-\beta}, \tag{3.42}$$

where

$$Y_1 = \frac{(2-\alpha)(l_1 + j_1)W_{+0}}{2(1-j_2)W_{+2}U}. \tag{3.43}$$

As before, Eqs. (3.8)–(3.10) (with $\hat{E}'=0$) can be solved for $\tilde{t}$ with the aid of Eq. (3.4) and, in this case, Eq. (2.4); an identical result to that of Sec. III B is encountered, namely,

$$\tilde{t}_{\mathrm{ci}} \approx T_p t. \tag{3.44}$$

The scaling densities are simply obtained by introducing Eqs. (3.42) and (3.44) in Eqs. (2.6) and (2.7) (for $\tilde{t}>0$)

$$\tilde{m}_{\mathrm{ci}} \approx \frac{l_1 + j_1}{1 - j_2}\frac{A^+}{1-\alpha}|T_p|^{-1}|t|^{1-\alpha}, \tag{3.45}$$

$$\tilde{s}_{\mathrm{ci}} \approx \frac{A^+}{1-\alpha}|T_p|^{-1}|t|^{1-\alpha}, \tag{3.46}$$

where

$$A^+ = (2-\alpha)(1-\alpha)QW_{+0}|T_p|^{2-\alpha} \tag{3.47}$$

is the critical amplitude of $\hat{C}_{V,E'}$ in the one-phase region. By substituting Eqs. (3.45) and (3.46) in Eq. (3.32) and expanding the denominator, we get Eq. (1.2), i.e.,

$$\varepsilon^{\mathrm{ci}}(T) = \varepsilon_c + \bar{E}_{1-\alpha}|t|^{1-\alpha} + \bar{E}_1|t| + \cdots, \tag{3.48}$$

where

$$\bar{E}_{1-\alpha} = -\frac{d\breve{T}_c}{d\breve{E}'}\frac{A^+}{1-\alpha}. \tag{3.49}$$

The $|t|^{1-\alpha}$ singularity was first advanced by Mistura [56] by applying the Fisher-Griffiths smoothness postulate [47,57,58] and, as noted in Sec. I, later obtained in SBMG algebraically. Indeed, the result (3.49) can be readily obtained via the exact thermodynamic relation

$$\hat{C}_{V,E'} = \hat{C}_{V,\varepsilon} + \frac{T}{Nk_B}\left(\frac{\partial S}{\partial \varepsilon}\right)_{T,V}\left(\frac{\partial \varepsilon}{\partial T}\right)_{V,E'}, \tag{3.50}$$

where $\hat{C}_{V,\varepsilon} \equiv T(\partial S/\partial T)_{V,\varepsilon}/Nk_B$. Hence, taking into account (i) that $\rho(\partial S/\partial \varepsilon)_{T,\rho} = -(\partial E'/\partial T)_{\rho,\varepsilon}$ (as follows from basic thermodynamics) and (ii) that at criticality $\hat{C}_{\varepsilon,V}$ is finite while $(\partial E'/\partial T)_{V,\varepsilon} = [dT_c/dE']^{-1}$, we find

$$\frac{d\breve{T}_c}{d\breve{E}'} = -T_c\frac{(\partial\varepsilon/\partial T)_{E',V}}{\hat{C}_{E',V}}. \tag{3.51}$$

This equation is valid asymptotically close to the critical point and combined with Eq. (3.48) yields Eq. (3.49).

## IV. THEORY FOR BINARY MIXTURES

Here, in addition to the liquid-gas phase transition, the possibility of liquid-liquid phase separation or demixing exists. In the former case, a second chemical potential acts—in addition to $E'$—as a nonordering field, while, as pointed out in Sec. II B, it is the pressure what plays such a role for the liquid-liquid phase transition. We shall focus our attention on the liquid-liquid case, for which there is a great number of accurate experimental studies in the literature. Many details of the derivation below will be omitted since it is analogous to that of Sec. III in many respects.

### A. Formulation and general expressions

According to the so-called principle of isomorphism [50], different phase transitions are thermodynamically equivalent in the critical region once proper analogies between variables are established. For the liquid-gas↔liquid-liquid case, we have $p \leftrightarrow -\mu_1$, $T \leftrightarrow T$, and $\mu \leftrightarrow \mu_{21}$. [Note also the equivalence between Eqs. (2.12) and (2.18) when the $vdp$ term is neglected.] Thus we may write

$$\tilde{h} \approx \hat{\mu}_{21}(p,E') - k_1^m(p,E')t(p,E') - j_2^m(p,E')[-\hat{\mu}_1(p,E')], \tag{4.1}$$

$$\tilde{t} \approx t(p,E') - l_1^m(p,E')\hat{\mu}_{21}(p,E') - j_1^m(p,E')[-\hat{\mu}_1(p,E')], \tag{4.2}$$

$$\tilde{g} \approx -\hat{\mu}_1(p,E') - k_0^m(p,E')t(p,E') - l_0^m(p,E')\hat{\mu}_{21}(p,E'). \tag{4.3}$$

Implicit is that the formulation is restricted to the $E=0$ case, where, recall, linear terms in $E$ vanish. Hence,

$$\tilde{h} \approx \hat{\mu}_{21} - k_1^m t - j_2^m(-\hat{\mu}_1) - i_2^m(-\hat{p}) - q_2'^m\hat{E}', \tag{4.4}$$

$$\tilde{t} \approx t - l_1^m\hat{\mu}_{21} - j_1^m(-\hat{\mu}_1) - i_1^m(-\hat{p}) - q_1'^m\hat{E}', \tag{4.5}$$

$$\tilde{g} \approx -\hat{\mu}_1 - k_0^m t - l_0^m\hat{\mu}_{21} - i_0^m(-\hat{p}) - q_0'^m\hat{E}' + \cdots. \tag{4.6}$$

The $p$ and $E'$ mixing coefficients read

$$i_2^m = -\left[j_2^m\rho_c\left(\frac{\partial\mu_{1,c}}{\partial p}\right)_{E'} + \rho_c\left(\frac{\partial\mu_{21,c}}{\partial p}\right)_{E'} - k_1^m k_B\rho_c\left(\frac{\partial T_c}{\partial p}\right)_{E'}\right], \tag{4.7}$$

$$i_1^m = -\left[j_1^m\rho_c\left(\frac{\partial\mu_{1,c}}{\partial p}\right)_{E'} - l_1^m\rho_c\left(\frac{\partial\mu_{21,c}}{\partial p}\right)_{E'} + k_B\rho_c\left(\frac{\partial T_c}{\partial p}\right)_{E'}\right], \tag{4.8}$$

$$i_0^m = -\left[-\rho_c\left(\frac{\partial\mu_{1,c}}{\partial p}\right)_{E'} - l_0^m\rho_c\left(\frac{\partial\mu_{21,c}}{\partial p}\right)_{E'} - k_0^m k_B\rho_c\left(\frac{\partial T_c}{\partial p}\right)_{E'}\right], \tag{4.9}$$

$$q_2'^m = -\left[-j_2^m\rho_c\left(\frac{\partial\mu_{1,c}}{\partial E'}\right)_p + \rho_c\left(\frac{\partial\mu_{21,c}}{\partial E'}\right)_p + k_1^m k_B\rho_c\left(\frac{\partial T_c}{\partial E'}\right)_p\right], \tag{4.10}$$

$$q_1'^m = -\left[-j_1^m\rho_c\left(\frac{\partial\mu_{1,c}}{\partial E'}\right)_p + l_1^m\rho_c\left(\frac{\partial\mu_{21,c}}{\partial E'}\right)_p - k_B\rho_c\left(\frac{\partial T_c}{\partial E'}\right)_p\right], \tag{4.11}$$

$$q_0'^m = -\left[\rho_c\left(\frac{\partial \mu_{1,c}}{\partial E'}\right)_p + l_0^m \rho_c\left(\frac{\partial \mu_{21,c}}{\partial E'}\right)_p + k_0^m k_B \rho_c\left(\frac{\partial T_c}{\partial E'}\right)_p\right], \tag{4.12}$$

where derivatives are made dimensionless as in the pure-fluid case [see Eqs. (3.27) and (3.28)]. As before (see also Ref. [15]), we see that pressure mixing and electric field mixing terms in the scaling fields originate from the pressure and electric field dependence of critical coordinates.

The $T_c = T_c(p, E')$ lambda surface is characterized by

$$t = \Lambda_p \hat{p} + \Lambda_{E'} \hat{E}' + \cdots, \tag{4.13}$$

from which

$$\left(\frac{\partial \breve{T}_c}{\partial \breve{p}}\right)_E \equiv k_B \rho_c \left(\frac{\partial T_c}{\partial p}\right)_E = -\frac{P_m}{T_m}, \tag{4.14}$$

$$\left(\frac{\partial \breve{T}_c}{\partial \breve{E}'}\right)_p \equiv k_B \rho_c \left(\frac{\partial T_c}{\partial E'}\right)_p = -\frac{E'_m}{T_m}, \tag{4.15}$$

where

$$P_m = l_1^m i_2^m + i_1^m + (j_1^m + j_2^m l_1^m)\frac{l_0^m i_2^m + i_0^m}{1 - j_2^m l_0^m}, \tag{4.16}$$

$$T_m = 1 - l_1^m k_1^m - (j_1^m + j_2^m l_1^m)\frac{k_0^m + k_1^m l_0^m}{1 - j_2^m l_0^m}, \tag{4.17}$$

$$E'_m = -\frac{(l_0^m q_2'^m + q_0'^m)(l_1^m j_2^m + j_1^m)}{1 - j_2^m l_0^m} - (l_1^m q_2'^m + q_1'^m). \tag{4.18}$$

Now, by introducing Eqs. (4.4)–(4.6) into Eq. (3.29) and comparing to Eq. (2.19), we get for the physical densities

$$\hat{s} = \frac{k_0^m - k_1^m \tilde{m} + \tilde{s}}{1 + j_2^m \tilde{m} + j_1 \tilde{s}}, \tag{4.19}$$

$$\hat{v} = \frac{i_0^m - i_2^m \phi_{1,m} - i_1^m \phi_{2,m}}{1 + j_2^m \phi_{1,m} + j_1^m \phi_{2,m}}, \tag{4.20}$$

$$x_2 = \frac{l_0^m + \tilde{m} - l_1^m \tilde{s}}{1 + j_2^m \tilde{m} + j_1^m \tilde{s}}, \tag{4.21}$$

$$\varepsilon = \frac{q_0'^m - q_2'^m \tilde{m} - q_1'^m \tilde{s}}{1 - i_2^m \tilde{m} - i_1^m \tilde{s}}. \tag{4.22}$$

### B. Two-phase region

As before, $\tilde{h}_\sigma = y_\sigma = 0$; however, since there is an extra thermodynamic degree of freedom we have, instead of a critical line, a two-dimensional surface of critical points. Therefore, in addition to $E=0$, another field must be specified. The most natural choice is to consider a path of approach to the critical point in which $p$ remains constant [i.e., $\hat{p}=0$ in Eqs. (4.4)–(4.6)]. We are thus faced with exactly the same mathematical problem as that of Sec. III, namely, to solve the expansions for the three scaling fields as a function of three physical fields. As a result, we find for $\tilde{t}$,

$$\tilde{t}_\sigma \approx T_m t, \tag{4.23}$$

where the mixing factor $T_m$, given by Eq. (4.17), is positive for UCPs and negative for LCPs.

The scaling densities are obtained by introducing Eq. (4.23) into Eqs. (2.6) and (2.7)

$$\tilde{m}_\sigma \approx \pm QUW_{-1}|T_m|^\beta |t|^\beta, \tag{4.24}$$

$$\tilde{s}_\sigma \approx -(2-\alpha)QW_{-0}|T_m|^{1-\alpha}|t|^{1-\alpha}. \tag{4.25}$$

These enter into Eq. (4.22) to give

$$\varepsilon^\pm(T) = \varepsilon_c \pm B_\varepsilon^m |t|^\beta [1 + e_\theta^m |t|^\theta + \cdots] + E_{2\beta}^m |t|^{2\beta} + E_{1-\alpha}^m |t|^{1-\alpha} + E_1^m |t| + \cdots, \tag{4.26}$$

where

$$B_\varepsilon^m = [\varepsilon_c i_2^m - q_2'^m] QUW_{-1}|T_m|^\beta, \tag{4.27}$$

$$E_\varepsilon^m = \frac{i_2^m (B_\varepsilon^m)^2}{\varepsilon_c i_2^m - q_2'^m}, \tag{4.28}$$

$$E_{1-\alpha}^m = [q_1'^m - \varepsilon_c i_1^m]\frac{A_m^-}{1-\alpha}|T_m|^{-1}, \tag{4.29}$$

in which it is implicit that $q_0'^m = \varepsilon_c$ while expressions for the remaining densities imply that $i_0^m = \hat{v}_c \equiv 1$, $k_0^m = \hat{s}_c$, and $l_0^m = x_{2,c}$ [15]. Again, + and − apply to the coexisting phases of different composition. In Eq. (4.29), $A_m^-$ represents the critical amplitude of the dimensionless isobaric heat capacity per particle at constant $x_2$ and electric field $\hat{C}_{p,x_2,E'} \equiv T(\partial S/\partial T)_{p,x_2,E'}/Nk_B$ in the two-phase region. By using the analogue of the Yang-Yang relation for a binary mixture, one gets (see Ref. [51])

$$A_m^- = (2-\alpha)(1-\alpha)QW_{-0}|T_m|^{2-\alpha}. \tag{4.30}$$

The diameter of the $\varepsilon - T$ coexistence curve follows from Eq. (4.26)

$$\varepsilon_d(T) = \varepsilon_c + E_{2\beta}^m |t|^{2\beta} + E_{1-\alpha}^m |t|^{1-\alpha} + E_1^m |t| + \cdots. \tag{4.31}$$

Again, this equation differs from that in SBMG [Eq. (1.1)] in that a $|t|^{2\beta}$ term dominating the anticipated $|t|^{1-\alpha}$ one is present. Such novel singularity depends on $p$ and $E'$ mixing into $\tilde{h}$ [see Eq. (4.28)], as it is the case of pure-fluid criticality [cf. Eq. (3.36) and related information]. But, remarkably, pressure acts here as a nonordering field, meaning that, in contrast to the pure-fluid case, a nonvanishing $|t|^{2\beta}$ contribution to $\varepsilon_d(T)$ does *not* imply the existence of the analogue of the Yang-Yang anomaly and related singularities in liquid-liquid criticality (see Refs. [13–15] for more details).

An alternative path of interest is defined by constant $T$. Equations (4.4)–(4.6) now give

$$\tilde{h}_{\sigma^*} \approx P_m \hat{p}, \tag{4.32}$$

where $P_m$ is given by Eq. (4.16). For a LCP, $P_m$ has the same sign as $(\partial T_c/\partial p)_{E'}$, whereas the opposite is true for a UCP [see Eq. (4.14)]. Accordingly, one can easily anticipate that the expressions for $\tilde{m}_{\sigma^*}$, $\tilde{s}_{\sigma^*}$, and $\varepsilon(p)$ differ from their counterparts along the above-studied path of constant $p$ and $E'$ by powers of the factor $|P_m/T_m|$, which identifies to $|(\partial \breve{T}_c/\partial \breve{p})_{E'}|$ [see Eq. (4.14)]. Accordingly, we obtain

$$\varepsilon^{\pm}(p) = \varepsilon_c \pm B^m_{\varepsilon^*}|\hat{p}|^{\beta}[1 + e^m_{\theta^*}] + E^m_{2\beta^*}|\hat{p}|^{2\beta} + E^m_{1-\alpha^*}|\hat{p}|^{1-\alpha} + E^m_{1^*}|\hat{p}| + \cdots , \tag{4.33}$$

where

$$B^m_{\varepsilon^*} = B^m_{\varepsilon}\left|\left(\frac{\partial \breve{T}_c}{\partial \breve{p}}\right)_{E'}\right|^{\beta}, \tag{4.34}$$

$$E^m_{2\beta^*} = E^m_{2\beta}\left|\left(\frac{\partial \breve{T}_c}{\partial \breve{p}}\right)_{E'}\right|^{2\beta}, \tag{4.35}$$

$$E^m_{1-\alpha^*} = E^m_{1-\alpha}\left|\left(\frac{\partial \breve{T}_c}{\partial \breve{p}}\right)_{E'}\right|^{1-\alpha}, \tag{4.36}$$

which indicate that the amplitudes change in magnitude but *not* in sign.

### C. Critical isopleth in the one-phase region

By analogy with Sec. III C, this path, to be labeled as "ci," is defined from Eq. (4.21). Using the same procedure that led to Eq. (3.42), one finds

$$y = Y_{1,m}|\tilde{t}|^{1-\alpha-\beta}, \tag{4.37}$$

where

$$Y_{1,m} = \frac{(2-\alpha)(l^m_1 + j^m_1 x_{2,c})W^0_{+0}}{2(1 - j^m_2 x_{2,c})W^0_{+2}U}. \tag{4.38}$$

We now proceed to solve Eqs. (4.4)–(4.6) for $\tilde{t}$ with the aid of Eq. (3.4); for a path of constant $p$, we obtain

$$\tilde{t}_{\mathrm{ci}} \approx T_m t. \tag{4.39}$$

Expressions for the scaling densities follow by combining Eqs. (4.37) and (4.39) with Eqs. (2.6) and (2.7):

$$\tilde{m}_{\mathrm{ci}} \approx Q(2-\alpha)\frac{l^m_1 + j^m_1 x_{2,c}}{1 - j^m_2 x_{2,c}} W_{+0}|T_m|^{1-\alpha}|t|^{1-\alpha} \tag{4.40}$$

and

$$\tilde{s}_{\mathrm{ci}} \approx \frac{A^+_m}{1-\alpha}|T_m|^{-1}|t|^{1-\alpha}, \tag{4.41}$$

where

$$A^+_m = (2-\alpha)(1-\alpha)QW^0_{+0}|T_m|^{2-\alpha} \tag{4.42}$$

is the critical amplitude of $\hat{C}_{p,x_2,E'}$ in the one-phase region.

By substituting Eqs. (4.40) and (4.41) into Eq. (4.22), we get

$$\varepsilon^{ic}(T) = \varepsilon_c + \bar{E}^m_{1-\alpha}|t|^{1-\alpha} + \bar{E}^m_1|t| + \cdots , \tag{4.43}$$

with

$$\bar{E}^m_{1-\alpha} = \mp\left[\left(\frac{\partial \breve{T}_c}{\partial \breve{E}'}\right)_p + \varepsilon_c\left(\frac{\partial \breve{T}_c}{\partial \breve{p}}\right)_{E'}\right]\frac{A^+_m}{1-\alpha}, \tag{4.44}$$

where − and + apply to UCPs and LCPs, respectively. (Recall that $T_m$ is positive for a UCP and negative for a LCP.) Equation (4.44) is no more than Eq. (1.3). To fully understand its origin, it will be helpful to obtain $\hat{\rho}^{\mathrm{ci}}(T) = [\hat{v}^{\mathrm{ci}}(T)]^{-1}$ and $[\hat{\rho}^{-1}\varepsilon]^{\mathrm{ci}}(T)$. From Eq. (4.20) we find

$$\hat{\rho}^{\mathrm{ci}}(T) = 1 + \bar{D}^m_{1-\alpha}|t|^{1-\alpha} + \bar{D}^m_1|t| + \cdots , \tag{4.45}$$

which, combined with Eq. (4.43), yields

$$[\hat{\rho}^{-1}\varepsilon]^{ic}(T) = \varepsilon_c + \bar{C}^m_{1-\alpha}|t|^{1-\alpha} + \bar{C}^m_1|t| + \cdots , \tag{4.46}$$

with

$$\bar{D}^m_{1-\alpha} = \mp\left(\frac{\partial \breve{T}_c}{\partial \breve{p}}\right)_{E'}\frac{A^+_m}{1-\alpha}, \tag{4.47}$$

$$\bar{C}^m_{1-\alpha} = \mp\left(\frac{\partial \breve{T}_c}{\partial \breve{E}'}\right)_{E'}\frac{A^+_m}{1-\alpha}, \tag{4.48}$$

where, again, − and + apply to UCPs and LCPs. We encounter that, as advanced previously [2], the critical amplitude of the $|t|^{1-\alpha}$ singularity splits up into a, say, intrinsic contribution, $\bar{C}^m_{1-\alpha}$, and a second one arising from the density

$$\bar{E}^m_{1-\alpha} = \bar{C}^m_{1-\alpha} + \varepsilon_c \bar{D}^m_{1-\alpha}. \tag{4.49}$$

As done in Sec. III C, a consistency proof of the results obtained for the $|t|^{1-\alpha}$ contribution comes from basic thermodynamics combined with Fisher-Griffiths smoothness postulate. First, we shall consider the so-called Mayer's generalized equation, conveniently written as

$$\hat{C}_{p,x_2,E'} = \hat{C}_{V,x_2,E'} - \frac{T}{\rho^2 k_B}\left(\frac{\partial p}{\partial T}\right)_{V,x_2,E'}\left(\frac{\partial \rho}{\partial T}\right)_{p,x_2,E'}, \tag{4.50}$$

where $\hat{C}_{V,x_2,E'} \equiv T(\partial S/\partial T)_{V,x_2,E'}$. At the critical point, $\hat{C}_{V,x_2,E'}$ is finite whereas $(\partial p/\partial T)_{V,x_2,E'} = [(\partial T_c/\partial p)_{E'}]^{-1}$. Thus, in the immediate neighborhood of the critical point, Eq. (4.50) turns into

$$\left(\frac{\partial \breve{T}_c}{\partial \breve{p}}\right)_{E'} = -T_c\frac{(\partial \hat{\rho}/\partial T)_{p,x_2,E'}}{\hat{C}_{p,x_2,E'}}, \tag{4.51}$$

which combines with Eq. (4.45) to yield Eq. (4.47). For the intrinsic contribution, we start from

$$\hat{C}_{p,x_2,E'} = \hat{C}_{p,x_2,\rho^{-1}\varepsilon} + \frac{T}{Nk_B}\left(\frac{\partial S}{\partial(\rho^{-1}\varepsilon)}\right)_{p,x_2,T}\left(\frac{\partial(\rho^{-1}\varepsilon)}{\partial T}\right)_{p,x_2,E'}, \tag{4.52}$$

where $\hat{C}_{p,x_2,\rho^{-1}\varepsilon} \equiv T(\partial S/\partial T)_{p,x_2,\rho^{-1}\varepsilon}$. By noting that $[\partial S/\partial(\rho^{-1}\varepsilon)]_{p,x_2,T}/N = -(\partial E'/\partial T)_{p,x_2,\rho^{-1}\varepsilon}$ and that at criticality $\hat{C}_{p,x_2,\rho^{-1}\varepsilon}$ remains finite while $(\partial E'/\partial T)_{p,x_2,\rho^{-1}\varepsilon} = [(\partial T_c/\partial E')_p]^{-1}$, we obtain

$$\left(\frac{\partial \breve{T}_c}{\partial \breve{E}'}\right)_p = -T_c\frac{[\partial(\hat{\rho}\varepsilon)/\partial T]_{p,x_2,E'}}{\hat{C}_{p,x_2,E'}}, \tag{4.53}$$

which combined with Eq. (4.46) gives Eq. (4.48).

Let us finally consider a path of constant $T$ and $E'$, for which Eqs. (4.4)–(4.6) yield

$$\tilde{h}_{\mathrm{ci}*} \approx P_m\hat{p}. \tag{4.54}$$

Hence we get

$$\varepsilon^{\mathrm{ci}}(p) = \varepsilon_c + \bar{E}^m_{1-\alpha*}|\hat{p}|^{1-\alpha} + \bar{E}^m_{1*}|\hat{p}| + \cdots, \tag{4.55}$$

where

$$\bar{E}^m_{1-\alpha*} = \bar{E}^m_{1-\alpha}\left|\left(\frac{\partial \breve{T}_c}{\partial \breve{p}}\right)_{E'}\right|^{1-\alpha}. \tag{4.56}$$

Again, we observe that the critical amplitudes change in magnitude but not in sign.

## V. EXPERIMENTAL TESTING

### A. Pure fluids

The work by Pestak and Chan for CO in 1981 [16] is, as far as we know, the only experimental study supporting the $|t|^{1-\alpha}$ singularity in the one-phase region for pure fluids. Since then, no significant novel results have been obtained. Nonetheless, reanalysis of accurate literature $\varepsilon$ data for four fluids, namely, sulfur hexafluoride ($SF_6$) [59], nitrogen ($N_2$), neon (Ne), and deuterated hydrogen (HD) [60], for the more interesting—in the actual context—two-phase region is in order. Originally, those data were converted to densities with a view to analyze the behavior of the $\rho-T$ coexistence-curve diameter at near criticality (see also Refs. [61–63]). In Weiner's study for $SF_6$, which was regarded as the first experimental evidence for a departure from the law of the rectilinear diameter, $\varepsilon$ was converted to $\rho$ by means of a separate experiment, which, as far as we are aware, was never published. On the other hand, Clausius-Mossotti equation was employed by Pestak and Chan. Since manipulation of data can lead to spurious effects, it is advisable to analyze $\varepsilon_d(T)$ directly, all the more so because there is a theoretical expression for it [Eq. (3.41)] derived from the actual scaling formulation.

TABLE I. Fitting coefficients of Eqs. (5.1)–(5.5) and standard deviations $\sigma$ for the studied pure fluids; $\varepsilon_c$ was taken as a fixed parameter.

| $\varepsilon_c$ | $100E_{2\beta}$ | $10E_{1-\alpha}$ | $10E_1$ | $10^8\sigma$ |
|---|---|---|---|---|
| | | $SF_6$ | | |
| 1.2603 | 6.40 | 2.352 | | 6 |
| 1.2603 | 15.32 | | | 35 |
| 1.2603 | | 4.028 | | 21 |
| 1.2603 | 8.77 | | 2.706 | 5 |
| 1.2603 | | 7.000 | −8.525 | 7 |
| | | $N_2$ | | |
| 1.1553 | 1.08 | 1.101 | | 0.001 |
| 1.1553 | 4.57 | | | 3 |
| 1.1553 | | 1.416 | | 0.3 |
| 1.1553 | 2.11 | | 1.289 | 0.009 |
| 1.1553 | | 2.212 | −1.320 | 0.01 |
| | | Ne | | |
| 1.0725 | 0.003 | 0.413 | | 0.001 |
| 1.0725 | 1.44 | | | 0.8 |
| 1.0725 | | 0.405 | | 0.001 |
| 1.0725 | 0.39 | | 0.478 | 0.003 |
| 1.0725 | | 0.382 | 0.035 | 0.001 |
| | | HD | | |
| 1.1026 | 0.41 | 0.431 | | 0.001 |
| 1.1026 | 1.57 | | | 0.08 |
| 1.1026 | | 0.592 | | 0.01 |
| 1.1026 | 0.74 | | 0.581 | 0.02 |
| 1.1026 | | 0.967 | −0.688 | 0.003 |

Original $\varepsilon$ data were fitted using five different approaches in which no more than two terms in Eq. (3.41) are considered simultaneously; we proceeded in this way since our aim is to elucidate whether or not a $|t|^{2\beta}$ term is necessary to describe the data. For the same reason, correction-to-scaling terms, which are unimportant as asymptotic behavior is concerned, were ignored. Hence,

$$\varepsilon_d^{\mathrm{I}}(T) = \varepsilon_c + E_{2\beta}|t|^{2\beta} + E_{1-\alpha}|t|^{1-\alpha}, \tag{5.1}$$

$$\varepsilon_d^{\mathrm{II}}(T) = \varepsilon_c + E_{2\beta}|t|^{2\beta}, \tag{5.2}$$

$$\varepsilon_d^{\mathrm{III}}(T) = \varepsilon_c + E_{1-\alpha}|t|^{1-\alpha}, \tag{5.3}$$

$$\varepsilon_d^{\mathrm{IV}}(T) = \varepsilon_c + E_{2\beta}|t|^{2\beta} + E_1|t|, \tag{5.4}$$

$$\varepsilon_d^{\mathrm{V}}(T) = \varepsilon_c + E_{1-\alpha}|t|^{1-\alpha} + E_1|t|. \tag{5.5}$$

The results for the fitting coefficients are shown in Table I. Figure 2 illustrates the performance of I–III for $SF_6$, $N_2$, Ne, and HD. Fits IV and V provide essentially the same description as fit I. The observed, small deviation from linearity for $N_2$ can be accounted for without including the $|t|^{2\beta}$ term (i.e., using III or V). Fit I provides an equally satisfactory description; however, fit II, in which a $|t|^{2\beta}$ alone is considered, is poor, significantly poorer than (its $|t|^{1-\alpha}$ counterpart) fit III. Similar behavior is encountered for $SF_6$; nevertheless, the $|t|^{2\beta}$ singularity carries much more weight since $\varepsilon_d(T)$ exhibits a substantially larger curvature close to criticality. (Note

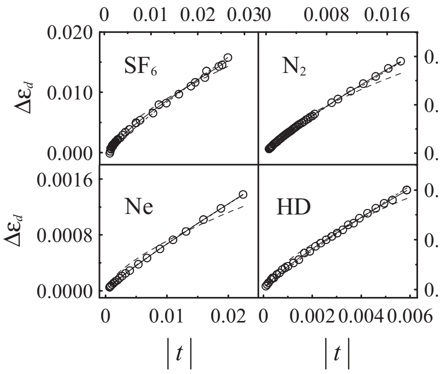

FIG. 2. Reduced coexistence-curve diameter $\Delta\varepsilon_d \equiv \varepsilon_d - \varepsilon_c$ as a function of the temperature critical deviation $|t|$ for all studied pure fluids (see text). Points are experimental data; lines are the calculated values using Eq. (5.1) (solid), Eq. (5.2) (long dashed), and Eq. (5.3) (short dashed); Eqs. (5.4) and (5.5), not shown here, provide essentially the same description as Eq. (5.1).

also that data for SF$_6$ lack the precision of those for the remaining fluids.) Values for effective critical exponents derived from log-log plots (Fig. 3) corroborate all these conclusions.

Therefore, despite experimental observations seem to indicate that the claimed $|t|^{2\beta}$ contribution to $\varepsilon_d(T)$ exists, evidence is not strong. Similar behavior has already been noted for $\rho_d(T)$ [9,10,65]. Conversely, experimental $C_V$ data in the two-phase region [66] point toward the existence of the Yang-Yang anomaly and so for pressure mixing into $\tilde{h}$ [see discussion below Eq. (3.41)]. On the basis that there exists additional reasons supporting pressure mixing [67], it is a possibility that the $|t|^{1-\alpha}$ and linear terms in Eq. (3.41) numerically mask the $|t|^{2\beta}$ contribution.

### B. Mixtures

Significant progress has been achieved in the 1980s as regards the experimental determination of $\varepsilon$ in the liquid-liquid critical region. One major advance has been the characterization of the Maxwell-Wagner effect, a low-frequency dispersion phenomenon occurring in heterogeneous media (like a system in the fluctuation-dominated critical region) because of the presence of ionic impurities. Specific work (see Refs. [17,18,30,68]) had to be done for mixtures with a view to overcome the difficulties arising from such effect.

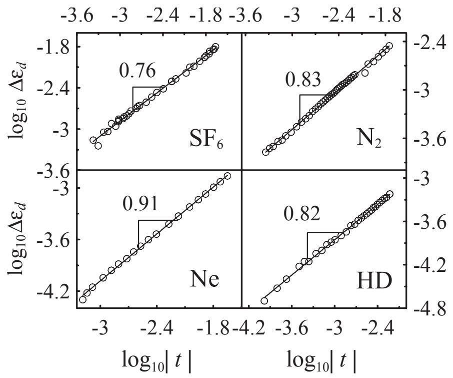

FIG. 3. Log-Log plots for all studied pure fluids (see text). Points are experimental data; solid lines are the fitted values to a straight line; slopes yield the values of the effective critical exponents [64].

TABLE II. Fitting coefficients of Eqs. (5.1)–(5.5) and standard deviations $\sigma$ for the studied binary mixtures; $\varepsilon_c$ was taken as a fixed parameter.

| $\varepsilon_c$ | $E_{2\beta}^m$ | $E_{1-\alpha}^m$ | $E_1^m$ | $10^3\sigma$ |
|---|---|---|---|---|
| | | BN-IO | | |
| 9.1036 | 6.697 | 15.482 | | 0.19 |
| 9.1036 | 13.268 | | | 3 |
| 9.1036 | | 30.948 | | 3 |
| 9.1036 | 8.538 | | 16.445 | 0.19 |
| 9.1036 | | 70.545 | −57.923 | 0.3 |
| | | NE-CH | | |
| 9.1866 | 13.457 | 24.170 | | 0.006 |
| 9.1866 | 19.208 | | | 0.1 |
| 9.1866 | | 78.887 | | 0.6 |
| 9.1866 | 15.052 | | 33.521 | 0.008 |
| 9.1866 | | 228.249 | −283.185 | 0.002 |
| | | NB-C12 | | |
| 15.6948 | 25.715 | −9.589 | | 1.0 |
| 15.6948 | 22.129 | | | 1.5 |
| 15.6948 | | 56.639 | | 27 |
| 15.6948 | 24.775 | | −11.055 | 1.0 |
| 15.6948 | | 243.086 | −287.510 | 1.6 |
| 18.1963[a] | 2.189[a] | −0.769 [a] | | 5 |
| 18.1963[a] | 1.266[a] | | | 27 |
| 18.1963[a] | | 1.014[a] | | 125 |
| 18.1963[a] | 1.965[a] | | −0.518[a] | 4 |
| 18.1963[a] | | 5.832[a] | −4.355[a] | 1.4 |

[a]These values are referred to data as a function of pressure and, therefore, correspond to $E_{i^*}^m$ (see text).

We shall begin by discussing the situation for the two-phase region. Attention will be focused on the accurate $\varepsilon_d(T)$ data by Kindt *et al.* [5] for benzonitrile-isooctane (BN-IO) and nitroethane-cyclohexane (NE-CH) and by Malik *et al.* [44] for nitrobenzene-dodecane (NB-C$_{12}$). They have been fitted using approaches I–V above (with $E_i$ being replaced by $E_i^m$). The resulting values for the fitting coefficients are shown in Table II, whereas the quality of fits I–III is graphically displayed in Fig. 4. As it can be observed, approaches I, IV, and V provide a good description for the three systems; however, the high values for the amplitudes in V may be a reflection of a large correlation between parameters. One is therefore led to conclude that the above data *indeed* support the existence of the $|t|^{2\beta}$ anomaly for liquid-liquid criticality. In fact, the best fits for NE-CH and NB-C$_{12}$ using a singular term alone are, in accord with the original analyses [5,6], those in which a $|t|^{2\beta}$ term is considered. The results for BN-IO suggest a smaller $|t|^{2\beta}$ anomaly. Figure 5 shows log-log plots: values for effective critical exponents are consistent with the above conclusions.

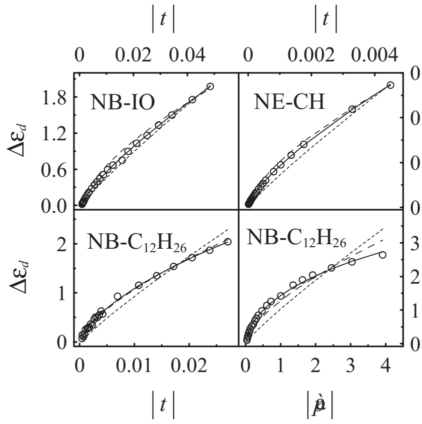

FIG. 4. Reduced coexistence-curve diameter $\Delta\varepsilon_d \equiv \varepsilon_d - \varepsilon_c$ as a function of the temperature critical deviation $|t|$ for all studied binary mixtures (see text); for NB-$C_{12}H_{26}$, data as a function of the pressure critical deviation $|\hat{p}|$ are also shown. Points are experimental data; lines are the calculated values using Eq. (5.1) (solid), Eq. (5.2) (long dashed), and Eq. (5.3) (short dashed); Eqs. (5.4) and (5.5), not shown here, provide essentially the same description as Eq. (5.1) except for NB-$C_{12}$ as a function of pressure (see text).

Even stronger evidence in favor of the $|\hat{p}|^{2\beta}$ singularity comes from the $\varepsilon_d(p)$ study by Malik *et al.* for NB-$C_{12}$ [44]. These data exhibit an *unusually* curved diameter (see Fig. 4) whose description *necessarily* requires a $|\hat{p}|^{2\beta}$ term: only approaches I, IV, and V work well whereas II and III are quite poor. To understand why $\varepsilon_d(p)$ displays a higher curvature than $\varepsilon_d(T)$, one must first note that $|(\partial\breve{T}_c/\partial\breve{p})_{E'}|<1$ for this system (see Table III). Accordingly, in going from $\varepsilon_d(T)$ to $\varepsilon_d(p)$, the amplitude of the contribution with exponent by $2\beta$ decreases to a lesser extent than those of the remaining, higher-order terms [see Eqs. (4.35) and (4.36)] since $|(\partial\breve{T}_c/\partial\breve{p})_{E'}|^{2\beta} > |(\partial\breve{T}_c/\partial\breve{p})_{E'}|^{1-\alpha} > |(\partial\breve{T}_c/\partial\breve{p})_{E'}|$. Such an enhanced visibility of the leading term for studies along the isothermal path has been noticed previously [40–44] and seems to be a general feature near ordinary liquid-liquid critical points. This may not be surprising since $|(\partial\breve{T}_c/\partial\breve{p})_{E'}|$ values are typically lesser than unity (see Table III).

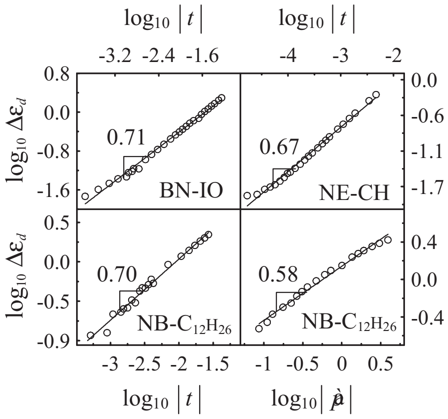

FIG. 5. Log-Log plots for all studied binary mixtures (see text). Points are experimental data and solid lines are the fitted values to a straight line; slopes yield the values for the effective critical exponents.

The majority of studies carried out along the critical isopleth in the one-phase region have unambiguously evidenced the existence of the $|t|^{1-\alpha}$ and $|\hat{p}|^{1-\alpha}$ singularities, which, as advanced in Sec. I, is a widely observed result. A deeper discussion of such a large amount of data entails looking at Eqs. (4.43) and (4.55). For that purpose, Table III contains values of all relevant parameters in those equations for some selected, representative systems. Critical coordinates $\rho_c$, $T_c$, $p_c$, and $\varepsilon_c$ as well as $(\partial\breve{T}_c/\partial\breve{E}')_p$ and $(\partial\breve{T}_c/\partial\breve{p})_{E'}$ values are also displayed. Whenever possible, $(\partial\breve{T}_c/\partial\breve{E}')_p$ has been calculated from $A_m^+$, $\varepsilon_c(\partial\breve{T}_c/\partial\breve{p})_{E'}$, and $\bar{E}^m_{1-\alpha}$ (or $\bar{E}^m_{1-\alpha^*}$) via Eq. (4.44). The results cannot be taken literally since $\bar{E}^m_{1-\alpha}$ and $\bar{E}^m_{1-\alpha^*}$ are subjected to a significantly large uncertainty inherent to separating terms with exponents closely spaced numerically (see, e.g., Ref. [84]); however, as we will explain below, they provide significant insights in a number of respects.

Our first remark is that the magnitude of the $|t|^{1-\alpha}$ singularity of $\varepsilon$ is, in general, significantly greater than that of $\rho$: one can verify that the anomalies are clearly visible in $\varepsilon$ vs $T$ plots (see the original papers as well as Fig. 6 for illustration). This is generally not the case for $\rho$ vs $T$ representations (see, e.g., Refs. [82,84,85] as well as literature data shown in Fig. 6), implying that $(\partial\breve{T}_c/\partial\breve{E}')_p$ is, typically, a large number as compared to $\varepsilon_c(\partial\breve{T}_c/\partial\breve{p})_{E'}$. Table III shows this fact, whose reliability can be checked by examining the results for nitrobenzene-isooctane (NB-IO) and A-CH, to the best of our knowledge the only systems for which experimental values of $(\partial\breve{T}_c/\partial\breve{E}')_p$ and $(\partial\breve{T}_c/\partial\breve{p})_{E'}$ are available. Hence, by calculating the $(\partial\breve{T}_c/\partial\breve{E}')_p$ of NB-IO through Eq. (4.44), one gets consistency, in terms of order of magnitude, with the experimental values directly obtained independently by Debye and Kleboth [31] and Orzechowski [34] (see Table III). On the other hand, the experimental value of $(\partial\breve{T}_c/\partial\breve{E}')_p$ for A-CH should lead to a very large anomaly in $\varepsilon$ which is not observed (in fact, $\bar{E}^m_{1-\alpha}$ vanishes within experimental uncertainty) [23]. We are inclined to think that typical values of $(\partial\breve{T}_c/\partial\breve{E}')_p$ are large, but not so large.

Second, for the same system, the anomaly in $\varepsilon(p)$ is stronger than that in $\varepsilon(T)$. As argued above, the singular contribution gains weight with respect to the linear one since $1 > |(\partial\breve{T}_c/\partial\breve{p})_{E'}|^{1-\alpha} > |(\partial\breve{T}_c/\partial\breve{p})_{E'}|$ and, consequently, the $|\hat{p}|^{1-\alpha}$ term is decreased to a lesser extent.

Finally, the calculated $(\partial\breve{T}_c/\partial\breve{E}')_p$ values are found to be negative in most of the studied cases. This is a consequence of the positive values for $\bar{E}^m_{1-\alpha}$ or $\bar{E}^m_{1-\alpha^*}$ [i.e., $\varepsilon$ curving downwards in a $\varepsilon_d$ vs $|t|$ (or $|\hat{p}|$) plot as the critical point is approached] and the negative ones (i.e., $\varepsilon$ bending upwards) are observed for UCPs and LCPs, respectively. Exceptions are A-CH, which, recall, shows an almost undetectable anomaly, and nitrobenzene-hexane (NB-$C_6$) along the isothermal path which, despite being of the UCP-type, exhibits a negative $\bar{E}^m_{1-\alpha^*}$ value. The behavior of NB-$C_6$ cannot be explained unless $(\partial\breve{T}_c/\partial\breve{E}')_p$ changes from negative to posi-

TABLE III. Critical coordinates, $\rho_c$ ($\mathrm{m}^{-3}$), $T_c$ (K), $p_c$ (MPa), and $\varepsilon_c$, slopes of the critical surface, and critical amplitudes involved in Eqs. (4.44) and (4.56).

| System[a] | $10^{-27}\rho_c$ | $T_c$ | $p_c$ | $\varepsilon_c$ | $(\partial\breve{T}_c/\partial\breve{E}')_p$ [b] | $\varepsilon_c(\partial\breve{T}_c/\partial\breve{p})_{E'}$ | $\bar{E}^m_{1-\alpha}$ | $\bar{E}^m_{1-\alpha^*}$ | $A^+_m$ |
|---|---|---|---|---|---|---|---|---|---|
| NB-$C_{12}$ | 4.009[e] | 302.65[f] | 0.1[f] | 15.60[f] | −0.96 | 0.0062[f] | 2.54[f] | | 2.35[g] |
| | 4.007[e] | 303.14[f] | 43.65[f] | 18.23[f] | −0.35 | 0.015[f] | | 0.96[f] | 2.35[c] |
| NB-$C_6$ | 5.132[e] | 292.65[h] | 0.1[h] | 10.88[f] | −1.29 | −0.139[h] | 2.18[e] | | 1.69[i] |
| | 5.156[e] | 288.55[h] | 28.9[h] | 10.70[h] | +0.50 | −0.074[h] | | −1.09[h] | 1.69[c] |
| NP-$C_{16}$ | 3.725[j] | 308.10[j] | 0.1[j] | 9.19[j] | −1.87 | 0.057[k] | 7.26[j] | | 3.36[d] |
| | 3.671[j] | 322.15[l] | 117.5[l] | 9.45[l] | −0.10 | 0.0581[l] | | 0.60[l] | 3.36[d,c] |
| NE-3MP | 5.922[m] | 299.69[n] | 0.1[n] | 9.73[n] | −3.40 | 0.029[o] | 11.4[n] | | 2.96[p] |
| TEA-W | 23.013[q] | 291.40[r] | 0.1[r] | 53.24[r] | −8.14 | 3.55[s] | −237[r] | | 45.9[t] |
| NB-IO | 4.508[u] | 302.21[v] | 0.1[v] | 10.28[v] | −3.22<br>[−7.74][w]<br>[−9.10][x] | −0.081[u] | 6.43[v] | | 1.83[u] |
| BN-IO | 4.350[y] | 291.69[z] | 0.1[z] | 9.14[z] | | −0.065[y] | 9.14[z] | | |
| A-CH | 5.905[s] | 286.39[aa] | 0.1[aa] | 3.71[aa] | ≈0<br>[−16391][ab] | 0.021[s] | ≈0[aa] | | 3.30[ac] |
| NE-CH | 6.496[ad] | 296.62[ae] | 0.1[ae] | 9.15[ae] | −4.70 | 0.12[af] | 13.9[af] | | 2.56[ad] |

[a] Abbreviated nomenclature: nitrobenzene-dodecane (NB-$C_{12}$), nitrobenzene-hexane (NB-$C_{12}$), nitropropane-hexadecane (NP-$C_{16}$), nitroethane-3-methyl-pentane (NE-3MP), triethylamine-water (TEA-W), nitrobenzene-isooctane (NB-IO); benzonitrile-isooctane (BN-IO), aniline-cyclohexane (A-CH), and nitroethane-cyclohexane (NE-CH).

[b] Calculated as indicated in the text.

[c] They have been assumed to be the same as those at atmospheric pressure.

[d] Unpublished data measured in Ourense laboratories.

[e] Reference [69].

[f] Reference [44].

[g] Reference [70].

[h] Reference [43].

[i] Reference [71].

[j] Reference [27].

[k] Reference [72].

[l] Reference [41].

[m] Reference [73].

[n] Reference [22].

[o] Reference [74].

[p] Reference [75].

[q] Reference [76].

[r] Reference [26].

[s] Reference [77].

[t] Reference [78].

[u] Reference [79].

[v] Reference [20].

[w] Reference [31].

[x] Reference [34].

[y] Reference [80].

[z] Reference [17].

[aa] Reference [23].

[ab] Reference [32].

[ac] Reference [81].

[ad] Reference [82].

[ae] Reference [18].

[af] Reference [83].

tive values (see Table III) in going from ($T_c = 292.65$ K, $p_c = 0.1$ MPa) to ($T_c = 288.55$ K, $p_c = 28.9$ MPa). Specific measurements for this system with a view to obtain $(\partial\breve{T}_c/\partial\breve{E}')_p$, $\varepsilon(p)$, and $\varepsilon(T)$ for those two points in the critical surface should shed light on this issue.

## VI. SUMMARY AND OUTLOOK

The thermodynamics of the dielectric constant $\varepsilon$ of fluids and fluid mixtures near fluid-fluid critical points has been updated. To this end, the traditionally accepted scaling formulation of near-critical fluid systems under an electric field has been extended according to the concept of complete scaling. While behavior in both the one-phase and two-phase regions is investigated, our main result is that coexistence-curve diameters in the $\varepsilon - T$ and $\varepsilon - p$ planes gain a leading $|Y|^{2\beta}$ (with $Y = t$ or $\hat{p}$) term. Pressure mixing and electric field mixing into the ordering field determine the strength of those

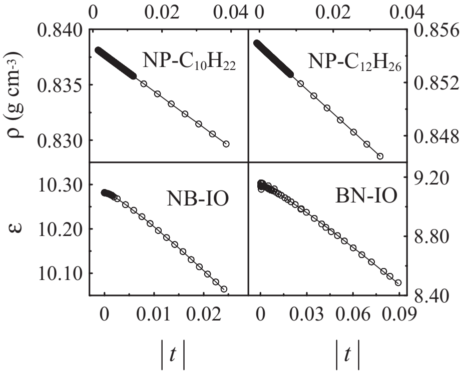

FIG. 6. Density $\rho$ and dielectric constant $\varepsilon$ in the one-phase region as a function of the temperature critical deviation $|t|$ for four binary mixtures (NP refers to nitropropane). Points are experimental data [84]; solid lines are fitted values.

anomalies, the former being responsible for its existence. From a purely thermodynamic perspective, the presence of the $|Y|^{2\beta}$ singularity for pure fluids is relevant in that it implies the existence of the Yang-Yang and related anomalies, while for liquid-liquid phase transitions such a term originates from the dependence of critical coordinates on pressure.

The analysis of available experimental data reveals good consistency with the theoretical results: in contrast to pure fluids, liquid-liquid binary systems provide strong evidence for the $|Y|^{2\beta}$ singularity. Moreover, the relation between $\varepsilon_d(T)$ and $\varepsilon_d(p)$ anomalies is driven by the dimensionless parameter $|(\partial \breve{T}_c / \partial \breve{p})_{E'}|$; the fact that it is typically lesser than 1 is consistent with the larger $\varepsilon_d(p)$ anomalies experimentally encountered. The same applies to $\varepsilon(T)$ and $\varepsilon(p)$ data along the critical isopleth in the one-phase region of liquid-liquid systems, where $\varepsilon(Y) \sim |Y|^{1-\alpha}$. No restrictions in both the sign and magnitude of the slope of the temperature-pressure-electric field critical surface in a plane of constant pressure should be expected. Nevertheless, information derived from $\varepsilon$ studies suggests that $(\partial \breve{T}_c / \partial \breve{E}')_p$ is usually negative.

Further experiments would be worthwhile. Additional studies in the two-phase region as well as measurements as a function of pressure should reinforce the actual conclusions. Experiments aimed at providing information on $(\partial \breve{T}_c / \partial \breve{E}')_p$, either via direct measurements or, indirectly, from $\varepsilon$ studies, are expected to be highly valuable. As explained at the end of Sec. V, nitrobenzene-hexane appears to be a promising candidate amenable to exhibit a topologically rich temperature-pressure-electric field critical surface.

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