

Critical Behavior of the Dielectric Constant in Asymmetric Fluids

C. E. Bertrand, J. V. Sengers,* and M. A. Anisimov

Institute for Physical Science & Technology and Department of Chemical & Biomolecular Engineering, University of Maryland, College Park, Maryland 20742, United States

ABSTRACT: By applying a thermodynamic theory that incorporates the concept of complete scaling, we derive the asymptotic temperature dependence of the critical behavior of the dielectric constant above the critical temperature along the critical isochore and below the critical temperature along the coexistence curve. The amplitudes of the singular terms in the temperature expansions are related to the changes of the critical temperature and the critical chemical potential upon the introduction of an electric field. The results of the thermodynamic theory are then compared with the critical behavior implied by the classical Clausius–Mossotti approximation. The Clausius–Mossotti approximation fails to account for any singular temperature dependence of the dielectric constant above the critical temperature. Below the critical temperature it produces an apparent asymmetric critical behavior with singular terms similar to those implied by the thermodynamic theory, but with significantly different coefficients. We conclude that the Clausius–Mossotti approximation only can account for the observed asymptotic critical behavior of the dielectric constant when the dependence of the critical temperature on the electric field is negligibly small.

INTRODUCTION

This paper is concerned with the asymmetric critical behavior of the dielectric constant of fluids. There are two major approaches in the literature to deal with the critical behavior of the dielectric constant, which we shall refer to as the thermodynamic theory and the Clausius–Mossotti approximation. The thermodynamic properties of systems near critical points exhibit singular behavior with universal critical exponents and universal scaling functions.^{1–3} A prototype for the universal critical behavior of fluids is the three-dimensional Ising model or its mathematical equivalent, the lattice gas.⁴ According to the principle of critical isomorphism,^{5–7} the critical behavior of fluids and fluid mixtures can be mapped onto the critical behavior of the Ising model, which is characterized by two independent scaling fields and one dependent scaling field (a thermodynamic potential). In the Ising model the critical behavior of the order parameter (spontaneous magnetization) is symmetric with respect to the ordering field (magnetic field). The types of critical phase transitions in fluids and fluid mixtures, including the observed asymmetric critical behavior of physical densities, are determined by the specific relationships between the Ising fields and the actual physical fields. Until recently it was thought that for fluids and fluid mixtures with N thermodynamic degrees of freedom, the two independent Ising scaling fields should be analytic functions of the N independent physical fields.^{8,9} This assumption, also referred to as revised scaling^{10,11} was based on some simple asymmetric models^{12–14} and on some empirical considerations of asymmetric asymptotic critical behavior of one-component fluids near the critical point.^{15–17} However, more recently it has been pointed out by Fisher and co-workers^{18–20} that for a proper description of critical phase transitions in fluids and fluid mixtures, all three Ising scaling fields should be taken as analytic functions of all physical fields, i.e., not only of the N independent physical fields but also of the remaining dependent physical field. This improved principle of critical isomorphic behavior is now

referred to as “complete scaling”. Complete scaling has indeed turned out to give a proper account of the observed asymmetric critical behavior of the density near the vapor–liquid critical point of one-component fluids^{21,22} and of the concentration in partially miscible liquid mixtures near the critical point of mixing.^{23–25}

The Clausius–Mossotti approximation starts from the well-known relation between the dielectric constant ε and the density ρ :

$$\frac{\varepsilon - 1}{\varepsilon + 2} = L\rho \quad (1)$$

In a similar manner, the square of the refractive index n is related to the density ρ by the Lorentz–Lorenz relation:

$$\frac{n^2 - 1}{n^2 + 2} = L'\rho \quad (2)$$

The Clausius–Mossotti function L and the Lorentz–Lorenz function L' are related to the effective polarizability and dipole moment of the molecules.^{26,27} Experiments show that L and L' are slowly varying functions of the density ρ and the temperature T .^{28–35} If one were to assume that the effective polarizability is not affected by critical fluctuations,³⁶ it follows that L and L' will remain slowly varying analytic functions of ρ and T near the critical point, which in a limited range of densities and temperatures can even be approximated by a constant.^{29,32,34} It then follows from eqs 1 and 2 that the critical behavior of the dielectric constant and of the refractive index is directly related to the critical behavior of the density. And indeed, measuring the dielectric constant or the refractive index has been widely used

Special Issue: H. Eugene Stanley Festschrift

Received: March 9, 2011

Revised: June 7, 2011

Published: June 30, 2011

as a method to determine the temperature dependence of the density near the critical point for many fluids.^{34,37–46}

In the thermodynamic theory of dielectric critical behavior, one adds the electric field as an additional physical field to be included in the relationship between the scaling fields. This procedure is supposed to yield the possible effect of critical fluctuations on the dielectric constant and should reduce to mean-field behavior if the fluctuations are neglected. Sengers et al.⁴⁷ have implemented this procedure in the revised-scaling approximation. This theory predicts that the dielectric constant along the critical isochore $\rho = \rho_c$ should contain a singular term proportional to $(T - T_c)^{1-\alpha}$, where ρ_c is the critical density, T_c is the critical temperature, and α is the critical exponent for the power-law divergence of the heat capacity, in agreement with earlier theoretical predictions of Mistura⁴⁸ and of Stell and Høye.⁴⁹ Several careful attempts have failed to find such a singular term in any nonpolar fluid within experimental resolution.^{50–52} Only for carbon monoxide has experimental evidence been reported for the presence of such a nonanalytic term as a function of temperature.^{53,54} Hence, it is commonly accepted that the Clausius–Mossotti approximation accounts for the critical behavior of the dielectric constant of nonpolar fluids but possibly not for polar fluids. The revised-scaling approximation leads to asymmetric critical behavior of the diameter of the dielectric constant in the two coexisting phases below the critical temperature with a leading singular term⁴⁷ proportional to $|T - T_c|^{1-\alpha}$, while the nonlinear relationship between dielectric constant and the density in the Clausius–Mossotti approximation causes a leading singular term in the diameter proportional to $|T - T_c|^{2\beta}$, where $\beta \approx 0.326$ is the exponent of the asymptotic critical power law for the order parameter.⁴⁹

In this paper we shall develop an improved thermodynamic theory by including the possible effect of critical fluctuations on the dielectric constant as a result of complete scaling. We shall compare the predicted critical behavior of the thermodynamic theory with that implied by the Clausius–Mossotti approximation that assumes that critical fluctuations do not directly affect the dielectric constant. In the actual implementation of the theory, we shall restrict ourselves to the dielectric constant of one-component fluids near the vapor–liquid critical point, although the theory can be readily extended to the dielectric constant of liquid mixtures near the critical point of mixing. Application of complete scaling to obtain the critical behavior of the dielectric constant of fluids has also recently been considered by Cerdeirina and co-workers.^{55,56} The primary purpose of the present paper is to elucidate the relationship between the thermodynamic theory and the Clausius–Mossotti approximation in a description of the critical behavior of the dielectric constant, an issue that has not been addressed by Cerdeirina and co-workers.^{55,56}

We shall proceed as follows. In the subsequent section we remind the reader of some relevant predictions for the thermodynamic behavior of fluids near the vapor–liquid critical point implied by complete scaling. We then consider the thermodynamics of a fluid subjected to an electric field and derive an expression for the critical behavior of the dielectric constant. Next we consider the critical behavior of the dielectric constant implied by the Clausius–Mossotti approximation. Specifically, we shall compare the asymmetric critical behavior of the dielectric constant predicted by the thermodynamic theory with the one resulting from the Clausius–Mossotti theory. In the final section we briefly summarize our conclusions.

COMPLETE SCALING IN FLUIDS NEAR THE VAPOR–LIQUID CRITICAL POINT

Fluids belong to the universality class of Ising-like systems whose critical behavior is characterized by two independent scaling fields—a “strong” scaling field h_1 (ordering field) and a “weak” scaling field h_2 —and by a dependent scaling field h_3 , which is a generalized homogeneous function of h_1 and h_2 . These scaling fields are defined such that at the critical point $h_1 = h_2 = h_3 = 0$. Associated with these scaling fields are two scaling densities: a strongly fluctuating scaling density ϕ_1 (order parameter), and a weakly fluctuating scaling density ϕ_2 , such that^{1,57}

$$\phi_1 = \left(\frac{\partial h_3}{\partial h_1} \right)_{h_2}, \quad \phi_2 = \left(\frac{\partial h_3}{\partial h_2} \right)_{h_1} \quad (3)$$

For positive values of h_2 , the system is uniform for all values of ϕ_1 . For negative values of h_2 , there is a region of two-phase equilibrium bounded by a coexistence curve where the order parameter asymptotically vanishes as

$$\phi_1 \approx \pm B_0 |h_2|^\beta \quad (h_2 \leq 0) \quad (4)$$

Along the path $h_1 = 0$, the weakly fluctuating scaling field varies as a function of h_2 as

$$\phi_2 = \frac{A_0^\pm}{1 - \alpha} |h_2|^{-\alpha} - B_{cr} h_2 \quad (5)$$

In these power laws, $\alpha \approx 0.110$ and $\beta \approx 0.326$ are two universal critical exponents, and A_0^\pm (A_0^+ for $h_2 \geq 0$ and A_0^- for $h_2 \leq 0$) and B_0 are critical amplitudes.^{1,57} The term with coefficient B_{cr} represents an analytic fluctuation-induced contribution to the weakly fluctuating density.^{11,58,59}

For fluids the physical fields are the temperature T , the pressure P , and the chemical potential μ (Gibbs energy per molecule) and the physical densities are the (molecular) number density ρ and the entropy density $s = \rho S$, where S is the entropy per molecule. It is convenient to introduce dimensionless fields and densities defined as

$$\hat{T} = \frac{T}{T_c}, \quad \hat{P} = \frac{P}{\rho_c k_B T_c}, \quad \hat{\mu} = \frac{\mu}{k_B T_c} \quad (6)$$

and

$$\hat{\rho} = \frac{\rho}{\rho_c}, \quad \hat{s} = \hat{\rho} \frac{S}{k_B} \quad (7)$$

where k_B is Boltzmann’s constant. Here we adopt the usual convention of designating the value of any thermodynamic quantity at the critical point by a subscript c. In addition we define

$$\Delta \hat{T} = \frac{T - T_c}{T_c}, \quad \Delta \hat{P} = \frac{P - P_c}{\rho_c k_B T_c}, \quad \Delta \hat{\mu} = \frac{\mu - \mu_c}{k_B T_c} \quad (8)$$

and

$$\Delta \hat{\rho} = \frac{\rho - \rho_c}{\rho_c}, \quad \Delta \hat{s} = \frac{s - s_c}{\rho_c k_B} \quad (9)$$

The prototype for the critical behavior of fluids is the lattice gas, which is a simple reformulation of the Ising model for one-component fluids.^{4,17,60} For the lattice gas, the ordering field h_1 is proportional to $\Delta \hat{\mu}$, the weak scaling field h_2 is proportional to $\Delta \hat{T}$, and the dependent scaling field is proportional to $\Delta \hat{\rho}$. As a consequence, ϕ_1 is proportional to $\Delta \hat{\rho}$, and ϕ_2 is proportional to

$\Delta\hat{s}$. The lattice gas is completely symmetric with respect to the critical isochore $\rho = \rho_c$. Real fluids do not exhibit perfect vapor–liquid symmetry. The principle of complete scaling asserts that for real fluids the Ising scaling fields are analytic functions of all physical fields, so that in first approximation^{18,20,22}

$$h_1 = a_1\Delta\hat{\mu} + a_2\Delta\hat{T} + a_3\Delta\hat{P} \quad (10)$$

$$h_2 = b_1\Delta\hat{T} + b_2\Delta\hat{\mu} + b_3\Delta\hat{P} \quad (11)$$

$$h_3 = c_1\Delta\hat{P} + c_2\Delta\hat{\mu} + c_3\Delta\hat{T} + c_{23}\Delta\hat{\mu}\Delta\hat{T} \quad (12)$$

In eq 12 we have retained a nonlinear contribution proportional to $\Delta\hat{\mu}\Delta\hat{T}$, since it will yield a linear contribution to the coexistence-curve diameter proportional to $\Delta\hat{T}$, as was already noticed earlier in the context of revised scaling.^{11,61} Complete scaling was proposed by Fisher and co-workers^{18–20} on a phenomenological basis inspired by a comment of Rehr and Mermin.¹⁰ Bertrand et al.^{62,63} have recently shown that complete scaling is consistent with the renormalization-group theory of critical phenomena in a first-order perturbation approximation.

As suggested by Wang and Anisimov²² and elaborated by Bertrand,⁶² by appropriate normalization of the scaling fields and by selecting a special value for the critical entropy, the matrix of coefficients in the expressions for the scaling fields can be expressed in terms of only three asymmetry coefficients a , b , and c :

$$a_1 = 1 - a, \quad a_2 = -\hat{s}_{ca}, \quad a_3 = a \quad (13)$$

$$b_1 = 1, \quad b_2 = b, \quad b_3 = 0 \quad (14)$$

$$c_1 = 1, \quad c_2 = -1, \quad c_3 = -\hat{s}_c, \quad c_{23} = c \quad (15)$$

so that

$$h_1 = \Delta\hat{\mu} + a[\Delta\hat{P} - \Delta\hat{\mu} - \hat{s}_c\Delta\hat{T}] \quad (16)$$

$$h_2 = \Delta\hat{T} + b\Delta\hat{\mu} \quad (17)$$

$$h_3 = [\Delta\hat{P} - \Delta\hat{\mu} - \hat{s}_c\Delta\hat{T}] + c\Delta\hat{\mu}\Delta\hat{T} \quad (18)$$

From the equations above, it follows that along the path $h_1 = 0$, the weak scaling field h_2 will asymptotically vary with temperature as^{11,20,25}

$$h_2 \approx \Delta\hat{T} \quad (19)$$

Since

$$d\hat{P} = \hat{s} d\hat{T} + \hat{\rho} d\hat{\mu} \quad (20)$$

one finds from eq 16–18 for the physical densities:^{11,22,62}

$$\hat{\rho} = \frac{1 + (1 - a)\varphi_1 + b\varphi_2 - c\Delta\hat{T}}{1 - a\varphi_1} \quad (21)$$

$$\hat{s} = \frac{\hat{s}_c(1 - a\varphi_1) + \varphi_2 - c\Delta\hat{\mu}}{1 - a\varphi_1} \quad (22)$$

At phase coexistence $h_1 = 0$ and $h_2 \leq 0$. Substituting power laws 4 and 5 for ϕ_1 and ϕ_2 into eq 21, using eq 19 for the relationship between h_2 and $\Delta\hat{T}$, and expanding the equation in terms of $\Delta\hat{T}$,

one finds^{11,22,62} for the asymptotic critical behavior of the coexisting vapor and liquid densities, ρ' and ρ'' ,

$$\frac{\hat{\rho}'' - \hat{\rho}'}{2} \equiv \Delta\hat{\rho}_{\text{cc}} \approx B_0|\Delta\hat{T}|^\beta \quad (23)$$

$$\begin{aligned} \frac{\hat{\rho}'' + \hat{\rho}'}{2} - 1 &\equiv \Delta\hat{\rho}_d \\ &\approx aB_0^2|\Delta\hat{T}|^{2\beta} - b\left[\frac{A_0^-}{1 - \alpha}|\Delta\hat{T}|^{1 - \alpha} - B_{\text{cr}}|\Delta\hat{T}|\right] \\ &\quad + c|\Delta\hat{T}| \end{aligned} \quad (24)$$

Equation 24 represents the coexistence-curve diameter. Complete scaling predicts^{18–20} that this diameter has a leading singularity proportional to $|\Delta\hat{T}|^{2\beta}$ as a result of the appearance of the pressure in the expression 16 for the ordering field. Using the same procedure one finds from eq 22 and eq 5 that, for $h_1 = 0$, $h_2 \geq 0$, $\Delta\hat{s}$ will vary asymptotically as

$$\Delta\hat{s} \approx \frac{A_0^+}{1 - \alpha}|\Delta\hat{T}|^{1 - \alpha} - B_{\text{cr}}|\Delta\hat{T}| \quad (25)$$

and for $h_1 = 0$, $h_2 \leq 0$

$$\Delta\hat{s} \approx -\left[\frac{A_0^-}{1 - \alpha}|\Delta\hat{T}|^{1 - \alpha} - B_{\text{cr}}|\Delta\hat{T}|\right] \quad (26)$$

In the one-phase region, the critical isochore $\Delta\hat{\rho} = 0$ coincides with the path $h_1 = 0$, $h_2 \geq 0$ asymptotically, so that eq 25 also represents the asymptotic power-law behavior of $\Delta\hat{s}$ when the critical point is approached in the one-phase region along the critical isochore.

CRITICAL BEHAVIOR OF A FLUID IN AN ELECTRIC FIELD

For a fluid subjected to an electric field \mathbf{E} we follow Mistura⁴⁸ and Sengers et al.⁴⁷ by adopting a potential $\Phi = P + \mathbf{D} \cdot \mathbf{E}$, where $\mathbf{D} = \epsilon\mathbf{E}$ is the electric induction. In principle \mathbf{D} and \mathbf{E} are vector quantities, but we restrict ourselves here to an isotropic system in which \mathbf{D} is in the same direction as the electric field \mathbf{E} , so that only their magnitudes D and E are relevant. Then the potential Φ is related to the pressure P by

$$\Phi = P + \epsilon E^2 \quad (27)$$

The potential satisfies the differential relation⁶⁴

$$d\Phi = s dT + \rho d\mu + \frac{\epsilon}{2} dE^2 \quad (28)$$

We shall apply the potential in the limit of a weak electric field $E \rightarrow 0$, where the dielectric constant will be independent of E . Consistent with the dimensionless thermodynamic quantities introduced in eqs 6 and 7 we define

$$\hat{\Phi} = \frac{\Phi}{\rho_c k_B T_c}, \quad \hat{E} = \frac{E}{\sqrt{2\rho_c k_B T_c}} \quad (29)$$

so that

$$d\hat{\Phi} = \hat{\rho} d\hat{\mu} + \hat{s} d\hat{T} + \epsilon d\hat{E}^2 \quad (30)$$

Our fundamental assumption is that a fluid in the presence of an electric field continues to belong to the Ising universality class. Arguments in favor of this assumption have been discussed by Sengers et al.⁴⁷ It is also closely related to the “smoothness

postulate” mentioned by Mistura.⁴⁸ To formulate complete scaling in the presence of an electric field, we generalize the physical field ΔP to the physical field $\Delta\Phi = \Phi - \Phi_c$, which reduces to ΔP in the limit $E \rightarrow 0$. We thus expect that the critical behavior of the potential Φ for a fluid in the presence of an electric field has the same mathematical form as the potential P in the absence of an electric field. Equation 30 can then be rewritten as

$$d[\Delta\hat{\Phi}(E)] = \hat{\rho} d[\Delta\hat{\mu}(E)] + \hat{s} d[\Delta\hat{T}(E)] \quad (31)$$

where $\Delta\hat{\Phi}(\hat{E}) = \hat{\Phi} - \hat{\Phi}_c(\hat{E})$, $\Delta\hat{\mu}(\hat{E}) = \hat{\mu} - \hat{\mu}_c(\hat{E})$, and $\Delta\hat{T}(\hat{E}) = \hat{T} - \hat{T}_c(\hat{E})$. Thus the electric field affects the critical behavior of the fluid not directly but through the dependence of the critical parameters on the electric field.^{65–72} The physical situation is analogous to the critical behavior of a weakly compressible liquid mixture near a critical point of mixing, where the pressure does not affect the critical fluctuations directly, but through the dependence of the critical parameters of the liquid mixture on the pressure.^{11,25} In the Appendix we show that complete scaling implies that the critical fields Φ_c , μ_c , and T_c must be analytic functions of the electric field E . For small E we may thus expand the field dependence of the critical fields in a Taylor series around $E = 0$ so as to obtain to first order in \hat{E}^2 :

$$d\hat{\Phi} = \hat{\rho} d\hat{\mu} + \hat{s} d\hat{T} + \left(\frac{d\hat{\Phi}_c}{d\hat{E}^2} - \hat{\rho} \frac{d\hat{\mu}_c}{d\hat{E}^2} - \hat{s} \frac{d\hat{T}_c}{d\hat{E}^2} \right) d\hat{E}^2 \quad (32)$$

which implies that

$$\varepsilon = \left(\frac{\partial \hat{\Phi}}{\partial \hat{E}^2} \right)_{\mu, T} = \frac{d\hat{\Phi}_c}{d\hat{E}^2} - \hat{\rho} \frac{d\hat{\mu}_c}{d\hat{E}^2} - \hat{s} \frac{d\hat{T}_c}{d\hat{E}^2} \quad (33)$$

From eq 30 we have

$$\frac{d\hat{\Phi}_c}{d\hat{E}^2} = \varepsilon_c + \frac{d\hat{\mu}_c}{d\hat{E}^2} + \hat{s}_c \frac{d\hat{T}_c}{d\hat{E}^2} \quad (34)$$

so that we obtain for $\Delta\varepsilon = \varepsilon - \varepsilon_c$

$$\Delta\varepsilon = - \left[\frac{d\hat{\mu}_c}{d\hat{E}^2} \Delta\hat{\rho} + \frac{d\hat{T}_c}{d\hat{E}^2} \Delta\hat{s} \right] \quad (35)$$

We shall refer to this expression as the thermodynamic theory of the dielectric constant, since it arises simply from the assumption of critical-point universality and holds independent of the specific relationship between the physical fields and the scaling fields. We conclude that the critical behavior of the dielectric constant is completely determined by the critical behavior of the density and entropy of the fluid in the absence of an electric field, but with amplitudes determined by the slopes of the critical locus as a function of the electric field, as already pointed out earlier by Mistura⁴⁸ on the basis of a similar general thermodynamic considerations and subsequently recovered by Sengers et al.⁴⁷

From a substitution of the complete scaling eqs 23, 24, and 26, derived in the previous section for the temperature dependence of $\Delta\hat{\rho}$ and $\Delta\hat{s}$, into eq 35 it follows immediately that the dielectric constants ε' and ε'' of the coexisting vapor and liquid phases have asymptotic temperature expansions of the form

$$\frac{\varepsilon'' - \varepsilon'}{2} \equiv \Delta\varepsilon_{\text{cxc}} \approx - \frac{d\hat{\mu}_c}{d\hat{E}^2} B_0 |\Delta\hat{T}|^\beta \quad (36)$$

$$\begin{aligned} \frac{\varepsilon'' - \varepsilon'}{2} - \varepsilon_c \equiv \Delta\varepsilon_d \approx & - \frac{d\hat{\mu}_c}{d\hat{E}^2} B_0^2 |\Delta\hat{T}|^{2\beta} \\ & + \left[\frac{d\hat{T}_c}{d\hat{E}^2} + b \frac{d\hat{\mu}_c}{d\hat{E}^2} \right] \left[\frac{A_0^-}{1-\alpha} |\Delta\hat{T}|^{1-\alpha} - B_{\text{cr}} |\Delta\hat{T}| \right] - \frac{d\hat{\mu}_c}{d\hat{E}^2} |\Delta\hat{T}| \end{aligned} \quad (37)$$

while the asymptotic temperature dependence of $\Delta\varepsilon$ along the critical isochore $\Delta\hat{\rho} = 0$ in the one-phase region is given by

$$\Delta\varepsilon \approx - \frac{d\hat{T}_c}{d\hat{E}^2} \left[\frac{A_0^+}{1-\alpha} |\Delta\hat{T}|^{1-\alpha} - B_{\text{cr}} |\Delta\hat{T}| \right] \quad (38)$$

We note that the $|\Delta\hat{T}|^{2\beta}$ contribution in expansion 37 of the dielectric-constant diameter arises from the density term in eq 35 and, hence, its amplitude is proportional to $d\hat{\mu}_c/d\hat{E}^2$. On the other hand, the $|\Delta\hat{T}|^{1-\alpha}$ contribution in eq 37 arises from both the density term and the entropy term in eq 35, and, hence, its amplitude contains both $d\hat{\mu}_c/d\hat{E}^2$ and $d\hat{T}_c/d\hat{E}^2$.

Equation 37 for the temperature dependence of dielectric-constant diameter has the same form as the one recently derived by Losada-Pérez et al.⁷³ A minor difference is that Losada-Pérez et al. identified the value of the dielectric constant at the critical point as $\varepsilon_c = q'_0$, where⁷⁴

$$q'_0 = \frac{d\hat{P}_c}{d\hat{E}^2} - \hat{s}_c \frac{d\hat{T}_c}{d\hat{E}^2} - \frac{d\hat{\mu}_c}{d\hat{E}^2} \quad (39)$$

However, $q'_0 = 0$, as can be seen by combining eq 34 with

$$\frac{d\hat{\Phi}_c}{d\hat{E}^2} = \varepsilon_c + \frac{d\hat{P}_c}{d\hat{E}^2} \quad (40)$$

which follows from eq 27. This deficiency is remedied if one identifies Φ , defined by eq 27, as the proper thermodynamic potential for a fluid in an electric field. The singular asymptotic temperature dependence, eq 38, for the dielectric constant along the critical isochore is identical to the one predicted by previous investigators,^{47–49,55} except that we have shown how an additional contribution linear in ΔT is related to a background contribution in the asymptotic temperature dependence of the isochoric specific heat capacity.

■ CLAUSIUS–MOSSOTTI APPROXIMATION

The Clausius–Mossotti relation (eq 1) between the dielectric constant ε and the density ρ arises from classical statistical mechanics. As such, it does not by itself present a theory of critical behavior, since it accounts only for noncritical short-range correlations. However, it does present an apparent theory of critical behavior if we assume that critical fluctuations do not contribute directly to the dielectric constant, but only indirectly through the dependence of the density on temperature in eq 1. As mentioned in the Introduction, a singular temperature dependence of the dielectric constant as predicted by eq 38 has not been observed for nonpolar fluids.^{50–52} This suggests that at least for nonpolar fluids the amplitudes of the singular contributions to the dielectric constant predicted by scaling are negligibly small and that the dominant contribution to the behavior of the dielectric constant arises from noncritical short-range contributions that in practice can be approximated by the Clausius–Mossotti relation.³⁶ And indeed, optical experiments in fluids near the critical point are commonly interpreted by assuming the

validity of the Lorentz–Lorenz relation (eq 2) for the refractive index, which is equivalent to the Clausius–Mossotti relation (eq 1) for the dielectric constant.^{38,40,44,62} Hence, it is of interest to investigate the critical behavior of the dielectric constant implied by the Clausius–Mossotti relation.

In principle the Clausius–Mossotti function L and the Lorentz–Lorenz function L' are analytic functions of temperature and density. However, there is considerable experimental evidence that for many fluids L and L' near the critical point are independent of temperature and slowly varying functions of the density alone.^{28–35} Thus in the Clausius–Mossotti approximation, $L(\hat{\rho})$, and hence $\varepsilon(\hat{\rho})$, are assumed to be analytic functions of density. One may then expand the dielectric constant near the critical point in a Taylor series in terms of $\Delta\hat{\rho}$:

$$\Delta\varepsilon = \varepsilon_1\Delta\hat{\rho} + \varepsilon_2(\Delta\hat{\rho})^2 + \dots \quad (41)$$

with coefficients

$$\varepsilon_1 = \frac{d\varepsilon}{d\hat{\rho}}, \quad \varepsilon_2 = \frac{d^2\varepsilon}{d\hat{\rho}^2} \quad (42)$$

where the derivatives are to taken at $\rho = \rho_c$. In a limited range of densities around the critical density L is often^{28,32,37,38,41,42,70} approximated by a constant $L = L_c$, so that

$$\begin{aligned} \varepsilon_c &= \frac{1 + 2L_c\rho_c}{1 - L_c\rho_c}, & \varepsilon_1 &= \frac{3}{1 - L_c\rho_c} \left(\frac{L_c\rho_c}{1 - L_c\rho_c} \right), \\ \varepsilon_2 &= \frac{3}{1 - L_c\rho_c} \left(\frac{L_c\rho_c}{1 - L_c\rho_c} \right)^2 \end{aligned} \quad (43)$$

As typical examples we may consider neon⁵¹ for which $L_c\rho_c = 0.026$ and $\varepsilon_1/\varepsilon_2 = 0.02$, nitrogen^{30,43} for which $L_c\rho_c = 0.050$ and $\varepsilon_1/\varepsilon_2 = 0.05$, and SF₆⁵² for which $L_c\rho_c = 0.084$ and $\varepsilon_1/\varepsilon_2 = 0.09$. Thus at least for nonpolar fluids eq 41 is a strongly convergent expansion.

If we substitute complete scaling expansions 23 and 24 for $\Delta\hat{\rho}$ into eq 41, we obtain for the temperature dependence of the dielectric constants ε' and ε'' of the coexisting vapor and liquid phases:

$$\frac{\varepsilon'' - \varepsilon'}{2} \equiv \Delta\varepsilon_{\text{cxc}} \approx \varepsilon_1 B_0 |\Delta\hat{T}|^\beta \quad (44)$$

$$\begin{aligned} \frac{\varepsilon'' - \varepsilon'}{2} - \varepsilon_c &\equiv \Delta\varepsilon_d \approx (\varepsilon_1 a + \varepsilon_2) B_0^2 |\Delta\hat{T}|^{2\beta} \\ &- \varepsilon_1 b \left[\frac{A_0^-}{1 - \alpha} |\Delta\hat{T}|^{1-\alpha} - B_{\text{cr}} |\Delta\hat{T}| \right] + \varepsilon_1 c \frac{d\hat{\mu}_c}{d\hat{E}^2} |\Delta\hat{T}| \end{aligned} \quad (45)$$

Thus the asymmetric critical behavior implied by the Clausius–Mossotti approximation for the dielectric constant along the phase boundary arises both from fluid asymmetry (through a , b , and c) and from the nonlinear relationship between ε and ρ (through ε_2). The Clausius–Mossotti approximation yields an asymmetric temperature dependence for the dielectric-constant diameter with the same types of singular terms as the thermodynamic theory given by eq 37. However, the amplitudes are significantly different. In particular, ε_2 appears as a coefficient in eq 45, so that even for a symmetric fluid ($a = b = c = 0$) the Clausius–Mossotti theory predicts a leading $|\Delta\hat{T}|^{2\beta}$ contribution to the dielectric-constant diameter. This is in sharp contrast to the thermodynamic theory that predicts a leading $|\Delta\hat{T}|^{2\beta}$ term

for a symmetric fluid and no $|\Delta\hat{T}|^{2\beta}$ contribution for a symmetric fluid. We note that attempts^{55,56} to demonstrate the presence of a singular term proportional to $|\Delta\hat{T}|^{2\beta}$ in the temperature expansion of the dielectric-constant diameter from experimental dielectric-constant data alone do not discriminate between the thermodynamic theory for the critical behavior of the dielectric constant and the Clausius–Mossotti approximation. In the absence of asymmetry in the fluid diameter ($a = b = c = 0$), there still would be a contribution proportional to $|\Delta\hat{T}|^{2\beta}$ due to the nonlinear relationship between ε and ρ , as has been originally pointed out by Høye and Stell.⁴⁹ Wang and Anisimov²² have provided evidence for pressure mixing for a number of one-component fluids based on dielectric-constant and refractive-index measurements. For the conversion of dielectric-constant data or refractive-index data to density data, the validity of the Clausius–Mossotti relation (eq 1) and of the Lorentz–Lorenz relation (eq 2) had been assumed.^{39,44} Hence, the analysis of Wang and Anisimov²² is implicitly based on the assumption that the temperature dependence of the dielectric-constant diameter is given by eq 45 rather than by eq 37.

■ COMPARISON BETWEEN THE THERMODYNAMIC THEORY AND CLAUSIUS–MOSSOTTI APPROXIMATION

To discriminate between the asymmetric critical behavior of the dielectric constant implied by the thermodynamic theory and that implied by the Clausius–Mossotti relation, it is essential that we consider the magnitude of the amplitudes of the singular contributions to the dielectric-constant diameter. Specifically, to compare the amplitudes of the singular terms in eq 45 with those in eq 37 we need an estimate for the derivatives of the critical chemical potential μ_c and the critical temperature T_c with respect to the electric field E . Such estimates are available in the literature.^{64,66,70} From the expression for the shift of the chemical potential due to the presence of the electric field, given by Landau and Lifshitz,⁶⁴ one finds

$$\frac{d\hat{\mu}_c}{d\hat{E}^2} = -\varepsilon_1 = -\frac{d\varepsilon}{d\hat{\rho}} \quad (46)$$

Hence, eq 44 for the difference between the dielectric constants of the coexisting vapor and liquid phases becomes

$$\frac{\varepsilon'' - \varepsilon'}{2} \equiv \Delta\varepsilon_{\text{cxc}} \approx -\frac{d\hat{\mu}_c}{d\hat{E}^2} B_0 |\Delta\hat{T}|^\beta \quad (47)$$

Thermodynamic expression 35 and Clausius–Mossotti approximation 41 are identical at linear order in $\Delta\rho$. Thus the Clausius–Mossotti approximation can be used in the asymptotic analysis of experimental dielectric-constant data along the phase boundary for determining the critical exponent β .

A calculation of $d\hat{T}_c/d\hat{E}^2$ is slightly more complicated. Using a mean-field equation of state, Landau and Lifshitz⁶⁴ have suggested that $d\hat{T}_c/d\hat{E}^2$ is proportional to $\varepsilon_2 = d^2\varepsilon/d\hat{\rho}^2$. Combining a scaling equation of state and the Clausius–Mossotti relation, Zimmerli et al.⁷⁰ have concluded that

$$\hat{T}_c(E) = \hat{T}_c(0) + (\Gamma_0 \varepsilon_2 \hat{E}^2)^{1/\gamma} \quad (48)$$

where Γ_0 is a constant and $\gamma = 2 - \alpha - 2\beta \approx 1.24$. According to this estimate \hat{T}_c would be a nonanalytic function of E and $d\hat{T}_c/d\hat{E}^2$ would diverge at the critical point which would violate the basic assumption that a fluid in the presence of a field continues to belong to the Ising universality class as shown in

the Appendix. The correct expression for $\hat{T}_c(E)$ that corresponds to the thermodynamic expression for the dielectric constant (eq 35) is written as

$$\hat{T}_c(E) = \hat{T}_c(0) + \frac{d\hat{T}_c}{d\hat{E}^2} \hat{E}^2 \quad (49)$$

where, as shown in the Appendix, $d\hat{T}_c/d\hat{E}^2$ is finite. We conclude that the Clausius–Mossotti theory is only valid when used in conjunction with a mean-field equation of state. Specifically, for a mean-field equation of state, $\gamma = 1$, $\Gamma_0 = 1/2$, and, as discussed by Landau and Lifshitz,⁶⁴ $\varepsilon_2 = 2(d\hat{T}_c/d\hat{E}^2)$, so that the Clausius–Mossotti expression for $\hat{T}_c(E)$ (eq 48) indeed reduces to eq 49. Furthermore, the thermodynamic theory (eq 35) reduces to the Clausius–Mossotti theory (eq 41) for a mean-field equation of state, since $\Delta\hat{\varepsilon} = -1/2(\Delta\hat{\rho}^2)$. Therefore, the thermodynamic theory encompasses the Clausius–Mossotti theory in the mean-field regime.

Even though the Clausius–Mossotti theory is only strictly correct for a mean-field equation of state, this does not necessarily imply that use of the Clausius–Mossotti relation to interpret dielectric-constant data will always introduce significant error. At least for nonpolar fluids, in which ε_1 is small, ε_2 will be an order of magnitude smaller than ε_1 , as mentioned earlier, and consequently $d\hat{T}_c/d\hat{E}^2$ is also expected to be small. We believe that this is also the reason why the singular temperature dependence of the dielectric constant along the critical isochore in the one-phase region in accordance with eq 38 has not been found experimentally for nonpolar fluids. For instance, Zimmerli et al.⁷⁰ have found that the shift of the critical temperature in SF₆ is unmeasurably small. We note that Hegsett and Amara⁷² have reported a larger effect in SF₆, but this result disagrees not only with the experiments of Zimmerli et al.,⁷⁰ but also with the measurements of Thijssse⁵² for SF₆. Hence, for nonpolar fluids it appears reasonable to approximate the asymptotic behavior of the dielectric constant along the phase boundary as a linear function of $\Delta\hat{\rho}$,

$$\Delta\varepsilon \approx -\frac{d\hat{\mu}_c}{d\hat{E}^2} \Delta\hat{\rho} \quad (50)$$

by neglecting the $d\hat{T}_c/d\hat{E}^2$ contribution in eq 35, or equivalently the ε_2 contribution in eq 41. In this approximation, the asymmetry in the diameter of the dielectric constant is proportional to that of the density. Differences between the Clausius–Mossotti theory and the thermodynamic theory for the critical behavior of the dielectric constant can be expected when $d\hat{T}_c/d\hat{E}^2$ is not small. In such a case, use of the Clausius–Mossotti relation to convert dielectric-constant data to density data, as is typically done in light-scattering experiments, would introduce to the density diameter $\Delta\hat{\rho}_d$ an artificial $|\Delta\hat{T}|^{2\beta}$ contribution proportional to $d\hat{T}_c/d\hat{E}^2$. For example, based on the CO data measured by Pestak and Chan,⁵³ one can estimate that $d\hat{T}_c/d\hat{E}^2 \sim \varepsilon_1 \sim \varepsilon_2 \sim 1$. An application of the Clausius–Mossotti approximation to CO would then lead to an underestimation of the asymmetry coefficient a and an overestimation of b . An observation of singular behavior of the dielectric constant in the one-phase region consistent with eq 38 would indicate that $d\hat{T}_c/d\hat{E}^2$ is not negligible and that an application of the Clausius–Mossotti approximation to dielectric-constant data in CO would introduce error.

DISCUSSION

The thermodynamic theory yields above T_c a singular contribution to the temperature dependence of the dielectric constant along the critical isochore proportional to $|\Delta\hat{T}|^{1-\alpha}$ in accordance with eq 38, which is absent in the Clausius–Mossotti approximation. Its amplitude is proportional to $d\hat{T}_c/d\hat{E}^2$ as was previously found in the revised-scaling approximation.⁴⁷ Hence, this term should be observable when $d\hat{T}_c/d\hat{E}^2$ is not small. We have found that below T_c the thermodynamic theory of the critical behavior of the dielectric constant and the Clausius–Mossotti approximation yield the same type of singular asymptotic critical behavior of the dielectric-constant diameter as a function of temperature. Both expansions include a term proportional to $|\Delta\hat{T}|^{2\beta}$ and a term proportional to $|\Delta\hat{T}|^{1-\alpha}$. However, the origins of these terms differ significantly. In the thermodynamic theory the $|\Delta\hat{T}|^{2\beta}$ contribution in eq 37 arises from the linear density term in eq 35 and has an amplitude proportional to $d\hat{\mu}_c/d\hat{E}^2$, while the Clausius–Mossotti approximation also yields a $|\Delta\hat{T}|^{2\beta}$ contribution in eq 45 arising from a nonlinear density contribution with an amplitude proportional to ε_2 and, hence, proportional to $d\hat{T}_c/d\hat{E}^2$ in the mean-field approximation. Furthermore, in the thermodynamic theory, the $|\Delta\hat{T}|^{1-\alpha}$ contribution in eq 37 arises from both the density term and the entropy term in eq 35 with amplitudes $d\hat{\mu}_c/d\hat{E}^2$ and $d\hat{T}_c/d\hat{E}^2$, respectively, while in the Clausius–Mossotti approximation the $|\Delta\hat{T}|^{1-\alpha}$ contribution arises only from the density, with any entropy contribution being neglected. In addition, the entropy term in eq 35 yields a singular contribution proportional to $|\Delta\hat{T}|^{1-\alpha}$ with amplitude $d\hat{T}_c/d\hat{E}^2$, which is absent in the Clausius–Mossotti approximation. The two approaches become identical in the mean-field approximation. However, in the critical region one should use eq 35 instead of the Clausius–Mossotti relation to extract the density from the dielectric constant. Additionally, the entropy coefficient $d\hat{T}_c/d\hat{E}^2$ in eq 35 can be found from eq 38 via measurements of the dielectric constant in the one-phase region along the critical isochore.

We have demonstrated that the Clausius–Mossotti approximation (eq 41) implies an unphysical nonanalytic $\hat{T}_c(E)$ and that the thermodynamic theory should be used instead. Fortunately, when $d\hat{T}_c/d\hat{E}^2$ is small, as is to be expected for nonpolar fluids, the linear approximation, eq 50 is consistent with both theories. Deviations in the critical behavior of the dielectric constant from the Clausius–Mossotti approximation can only be expected when $d\hat{T}_c/d\hat{E}^2$ is large, as may be the case for highly nonpolar fluids.

Cordeirina and co-workers^{55,56} have derived a temperature expansion of the dielectric-constant diameter near the critical point of mixing in liquid mixtures, similar to eq 37 and have found evidence for the presence of a $|\Delta\hat{T}|^{2\beta}$ term from experimental dielectric constant data. Again the presence of a $|\Delta\hat{T}|^{2\beta}$ term by itself does not discriminate between the thermodynamic theory including possible critical fluctuation effects and a Clausius–Mossotti approximation. Hence, to obtain a more physical picture of the nature of the asymmetric critical behavior of the dielectric constant in liquid mixtures, an analysis of the amplitudes of the singular contributions and their relationship with the electric-field dependence of the critical chemical potential versus that of the critical temperature will be needed.

APPENDIX: DEPENDENCE OF THE CRITICAL PARAMETERS ON THE ELECTRIC FIELD

We consider a fluid in the presence of an electric field. For systems belonging to the universality class of Ising-like systems,

complete scaling asserts that the Ising scaling fields are analytic functions of all physical fields. In linear approximation (cf. eqs 10–12 for a fluid in the absence of an electric field):

$$h_1 = a_1 \Delta \hat{\mu} + a_2 \Delta \hat{T} + a_3 \Delta \hat{\Phi} + a_4 \hat{E}^2 \quad (51)$$

$$h_2 = b_1 \Delta \hat{T} + b_2 \Delta \hat{\mu} + b_3 \Delta \hat{\Phi} + b_4 \hat{E}^2 \quad (52)$$

$$h_3 = c_1 \Delta \hat{\Phi} + c_2 \Delta \hat{\mu} + c_3 \Delta \hat{T} + c_4 \hat{E}^2 \quad (53)$$

In applying complete scaling we consider the fluid in the absence of an electric field as the reference state. Hence, in these equations $\Delta \hat{\mu}$, $\Delta \hat{T}$, and $\Delta \hat{\Phi}$ are to be interpreted as $\Delta \hat{\mu} = \hat{\mu} - \hat{\mu}_c(0)$, $\Delta \hat{T} = \hat{T} - \hat{T}_c(0)$, and $\Delta \hat{\Phi} = \hat{\Phi} - \hat{\Phi}_c(0) = \hat{\Phi} - \hat{P}_c(0)$. Everywhere on the critical locus $h_1 = h_2 = h_3 = 0$. Thus it follows from eq 51 to 53 that for $\hat{\mu} = \hat{\mu}_c(\hat{E})$, $\hat{T} = \hat{T}_c(\hat{E})$, and $\hat{\Phi} = \hat{\Phi}_c(\hat{E}) = \hat{P}_c(\hat{E}) + \varepsilon \hat{E}^2$:

$$a_1[\hat{\mu}_c(\hat{E}) - \hat{\mu}_c(0)] + a_2[\hat{T}_c(\hat{E}) - \hat{T}_c(0)] + a_3[\hat{\Phi}_c(\hat{E}) - \hat{P}_c(0)] + a_4 \hat{E}^2 = 0 \quad (54)$$

$$b_1[\hat{T}_c(\hat{E}) - \hat{T}_c(0)] + b_2[\hat{\mu}_c(\hat{E}) - \hat{\mu}_c(0)] + b_3[\hat{\Phi}_c(\hat{E}) - \hat{P}_c(0)] + b_4 \hat{E}^2 = 0 \quad (55)$$

$$c_1[\hat{\Phi}_c(\hat{E}) - \hat{P}_c(0)] + c_2[\hat{\mu}_c(\hat{E}) - \hat{\mu}_c(0)] + c_3[\hat{T}_c(\hat{E}) - \hat{T}_c(0)] + c_4 \hat{E}^2 = 0 \quad (56)$$

These equations can readily be solved for \hat{T}_c and $\hat{\mu}_c$ as a function of \hat{E}^2 :

$$\frac{d\hat{T}_c}{d\hat{E}^2} = \frac{(a_3 b_4 - a_4 b_3)(a_3 c_2 - a_1 c_1) - (a_3 b_2 - a_1 b_3)(a_3 c_4 - a_4 c_1)}{(a_3 b_2 - a_1 b_3)(a_3 c_3 - a_2 c_1) - (a_3 b_1 - a_2 b_3)(a_3 c_2 - a_1 c_1)} + O(\hat{E}^2) \quad (57)$$

$$\frac{d\hat{\mu}_c}{d\hat{E}^2} = \frac{(a_3 b_4 - a_4 b_3)(a_3 c_3 - a_2 c_1) - (a_3 b_1 - a_2 b_3)(a_3 c_4 - a_4 c_1)}{(a_3 b_1 - a_2 b_3)(a_3 c_2 - a_1 c_1) - (a_3 b_2 - a_1 b_3)(a_3 c_3 - a_2 c_1)} + O(\hat{E}^2) \quad (58)$$

Thus complete scaling implies that the critical temperature and the critical chemical potential are analytic functions of the electric field.

Just as in the case of a fluid in the absence of an electric field, the matrix of coefficients in eq 51 to 53 can be expressed in terms of only two independent asymmetry coefficients a and b with the aid of eq 13 to 15 and by identifying the coefficients a_4 , b_4 , and c_4 as

$$a_4 = -(1-a) \frac{d\hat{\mu}_c}{d\hat{E}^2} + \hat{s}_c \frac{d\hat{T}_c}{d\hat{E}^2} - a \frac{d\hat{\Phi}_c}{d\hat{E}^2} \quad (59)$$

$$b_4 = -\frac{d\hat{T}_c}{d\hat{E}^2} - b \frac{d\hat{\mu}_c}{d\hat{E}^2} \quad (60)$$

$$c_4 = -\frac{d\hat{\Phi}_c}{d\hat{E}^2} + \frac{d\hat{\mu}_c}{d\hat{E}^2} + \hat{s}_c \frac{d\hat{T}_c}{d\hat{E}^2} \quad (61)$$

The term $c_{23} \Delta \hat{\mu} \Delta \hat{T} = c \Delta \hat{\mu} \Delta \hat{T}$ in eq 12 is a nonlinear term that can be added to eq 53.

It is interesting to note that complete scaling is neutral as to whether the dependence of the critical values of the densities, like $\hat{\rho}_c$ and \hat{s}_c , on the electric field is analytic or nonanalytic. An

interesting example is the case of an ionic solute in a nonionic solvent.⁷⁵ The relevant physical fields for such a solution are the temperature, pressure, the chemical potential μ_1 of the solvent, and the difference μ_{21} between the chemical potentials of the solute and the solvent.^{11,24} Kim and Fisher⁷⁵ have shown that for a salt solution the critical temperature and the critical pressure become nonanalytic functions of the salt concentration. Nevertheless, one can readily show, using arguments similar to those given above, that even in this case the critical pressure will be an analytic function of the temperature.

AUTHOR INFORMATION

Corresponding Author

*E-mail: sengers@umd.edu.

ACKNOWLEDGMENT

The authors have benefitted from many discussions with Claudio A. Cerdeirina. The authors thank Dick Bedeaux for a critical reading of the manuscript. This research is supported by the Division of Chemistry of the National Science Foundation (Grant No. CHE-1012052).

REFERENCES

- (1) Fisher, M. E. In *Critical Phenomena*; Hahne, F. J. W., Ed.; Lecture Notes in Physics; Springer: Berlin, 1982; Vol. 186, p 1.
- (2) Stanley, H. E. *Rev. Mod. Phys.* **1999**, *71*, S358.
- (3) Kadanoff, L. P. In *The Oxford Handbook of Philosophy of Physics*; Batterman, R., Ed.; Oxford University Press: Oxford, 2011; in press.
- (4) Fisher, M. E. *Rep. Prog. Phys.* **1967**, *30* (II), 615.
- (5) Griffiths, R. B.; Wheeler, J. C. *Phys. Rev. A* **1970**, *2*, 1047.
- (6) Saam, W. F. *Phys. Rev. A* **1970**, *2*, 1461.
- (7) Anisimov, M. A.; Voronel, A. V.; Gorodetskii, E. E. *Sov. Phys. JETP* **1971**, *33*, 605.
- (8) Ley-Koo, M.; Green, M. S. *Phys. Rev. A* **1981**, *23*, 2650.
- (9) Anisimov, M. A.; Gorodetskii, E. E.; Kulikov, V. D.; Sengers, J. V. *Phys. Rev. E* **1995**, *51*, 1199.
- (10) Rehr, J. J.; Mermin, N. D. *Phys. Rev. A* **1973**, *8*, 472.
- (11) Behnejad, H.; Sengers, J. V.; Anisimov, M. A. In *Applied Thermodynamics*; Goodwin, A. H., Sengers, J. V., Peters, C. J., Eds.; IUPAC/RSC Publishing: Cambridge, U.K., 2010; p 321.
- (12) Widom, B.; Rowlinson, J. S. *J. Chem. Phys.* **1970**, *52*, 1670.
- (13) Mermin, N. D. *Phys. Rev. Lett.* **1971**, *26*, 169.
- (14) Mermin, N. D. *Phys. Rev. Lett.* **1971**, *26*, 957.
- (15) Vicentini-Missoni, M.; Levelt Sengers, J. M. H.; Green, M. S. *J. Res. Natl. Bureau of Standards* **1969**, *73A*, 563.
- (16) Levelt Sengers, J. M. H. *Ind. Eng. Chem. Fundam.* **1970**, *9*, 470.
- (17) Sengers, J. V.; Levelt Sengers, J. M. H. In *Liquid Physics*; Croxton, C. A., Ed.; Wiley: New York, 1978; p 163.
- (18) Fisher, M. E.; Orkoulas, G. *Phys. Rev. Lett.* **2000**, *85*, 696.
- (19) Orkoulas, G.; Fisher, M. E.; Üstün, C. J. *Chem. Phys.* **2000**, *113*, 7530.
- (20) Kim, Y. C.; Fisher, M. E.; Orkoulas, G. *Phys. Rev. E* **2003**, *67*, 061506.
- (21) Anisimov, M. A.; Wang, J. T. *Phys. Rev. Lett.* **2006**, *97*, 025703.
- (22) Wang, J. T.; Anisimov, M. A. *Phys. Rev. E* **2007**, *75*, 051107.
- (23) Cerdeirina, C. A.; Anisimov, M. A.; Sengers, J. V. *Chem. Phys. Lett.* **2006**, *424*, 414.
- (24) Wang, J. T.; Cerdeirina, C. A.; Anisimov, M. A.; Sengers, J. V. *Phys. Rev. E* **2008**, *77*, 031127.
- (25) Pérez-Sánchez, G.; Losada-Pérez, P.; Cerdeirina, C. A.; Sengers, J. V.; Anisimov, M. A. *J. Chem. Phys.* **2010**, *132*, 154502.
- (26) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1954.

- (27) Høye, J. S.; Bedeaux, D. *Physica A* **1977**, *87*, 288.
- (28) Lucas, J. M.; Smith, B. L. *Phys. Lett.* **1965**, *19*, 22.
- (29) Garside, D. H.; Mølgaard, H. V.; Smith, B. L. *J. Phys. B* **1968**, *1*, 449.
- (30) Ely, J. F.; Straty, G. C. *J. Chem. Phys.* **1974**, *61*, 1480.
- (31) Balzarini, D.; Palfy, P. *Can. J. Phys.* **1974**, *52*, 2007.
- (32) Burton, M.; Balzarini, D. *Can. J. Phys.* **1974**, *52*, 2011.
- (33) Beysens, D.; Calmettes, P. *J. Chem. Phys.* **1977**, *66*, 766.
- (34) Palfy-Muhoray, P.; Balzerini, D. *Can. J. Phys.* **1978**, *56*, 1140.
- (35) Närger, U.; Balzerini, D. A. *Phys. Rev. B* **1990**, *42*, 6651.
- (36) Larsen, S. Y.; Mountain, R. D.; Zwanzig, Z. *J. Chem. Phys.* **1963**, *42*, 2187.
- (37) Balzarini, D.; Ohrn, K. *Phys. Rev. Lett.* **1972**, *29*, 840.
- (38) Balzarini, D. A. *Can. J. Phys. (Paris)* **1972**, *50*, 2194.
- (39) Weiner, J.; Langley, K. H.; Ford, N. C., Jr. *Phys. Rev. Lett.* **1974**, *32*, 879.
- (40) Hocken, R.; Moldover, M. R. *Phys. Rev. Lett.* **1976**, *37*, 29.
- (41) Balzarini, D.; Burton, M. *Can. J. Phys.* **1979**, *57*, 1516.
- (42) Balzarini, D.; Mouritsen, O. G. *Phys. Rev. A* **1983**, *28*, 3515.
- (43) Pestak, M. W.; Chan, M. H. W. *Phys. Rev. B* **1984**, *30*, 274.
- (44) Pestak, M. W.; Goldstein, R. E.; Chan, M. H. W.; de Bruyn, J. R.; Balzerini, D. A.; Ashcroft, N. W. *Phys. Rev. B* **1987**, *36*, 599.
- (45) De Bruyn, J. R.; Balzerini, D. A. *Phys. Rev. B* **1989**, *39*, 9243.
- (46) Närger, U.; Balzarini, D. A. *Phys. Rev. B* **1989**, *39*, 9330.
- (47) Sengers, J. V.; Bedeaux, D.; Mazur, P.; Greer, S. C. *Physica A* **1980**, *104*, 573.
- (48) Mistura, L. *J. Chem. Phys.* **1973**, *59*, 4563.
- (49) Stell, G.; Høye, J. S. *Phys. Rev. Lett.* **1974**, *33*, 1268.
- (50) Doiron, T.; Meyer, H. *Phys. Rev. B* **1978**, *17*, 2141.
- (51) Chan, M. H. W. *Phys. Rev. B* **1980**, *21*, 1187.
- (52) Thijssse, B. J. *J. Chem. Phys.* **1981**, *74*, 4678.
- (53) Pestak, M. W.; Chan, M. H. W. *Phys. Rev. Lett.* **1981**, *46*, 943.
- (54) Pestak, M. W.; Chan, M. H. W. In *Proceedings of the 8th Symposium on Thermophysical Properties*; Sengers, J. V., Ed.; American Society of Mechanical Engineers: New York, 1982; Vol. I, p 467.
- (55) Losada-Pérez, P.; Pérez-Sánchez, G.; Cerdereña, C. A.; Thoen, J. *Phys. Rev. E* **2010**, *81*, 041121.
- (56) Leys, J.; Losada-Pérez, P.; Corodiyannis, G.; Cerdereña, C. A.; Thoen, J. *J. Chem. Phys.* **2010**, *132*, 104508.
- (57) Pelissetto, A.; Vicari, E. *Phys. Rep.* **2002**, *368*, 549.
- (58) Bagnuls, C.; Bervillier, C. *Phys. Rev. B* **1985**, *32*, 7209.
- (59) Anisimov, M. A.; Kiselev, S. B.; Sengers, J. V.; Tang, S. *Physica A* **1992**, *188*, 487.
- (60) Lee, T. D.; Yang, C. N. *Phys. Rev.* **1952**, *87*, 410.
- (61) Sengers, J. V.; Levelt Sengers, J. M. H. *Int. J. Thermophys.* **1984**, *5*, 195.
- (62) Bertrand, C. E. *Asymmetric Fluid Criticality*. P.D. Thesis, University of Maryland, College Park, MD, 2011.
- (63) Bertrand, C. E.; Nicoll, J. F.; Anisimov, M. A. To be submitted for publication.
- (64) Landau, L. D.; Lifshitz, E. M. *Electrodynamics of Continuous Media*; Pergamon: New York, 1960.
- (65) Debye, P.; Kleboth, K. *J. Chem. Phys.* **1965**, *42*, 3155.
- (66) Voronel', A. V.; Gitterman, M. Sh. *Sov. Phys. JETP* **1969**, *28*, 1306.
- (67) Onuki, A. *Europhys. Lett.* **1995**, *29*, 611.
- (68) Beaglehole, D. *J. Chem. Phys.* **1981**, *74*, 5251.
- (69) Wirtz, D.; Fuller, G. G. *Phys. Rev. Lett.* **1993**, *71*, 2236.
- (70) Zimmerli, G. A.; Wilkinson, R. A.; Ferrell, R. A.; Moldover, M. R. *Phys. Rev. E* **1999**, *59*, 5862.
- (71) Zimmerli, G. A.; Wilkinson, R. A.; Ferrell, R. A.; Moldover, M. R. *Phys. Rev. Lett.* **1999**, *82*, 5253.
- (72) Hegseth, J.; Amara, K. *Phys. Rev. Lett.* **2004**, *93*, 057402.
- (73) See eq 3.41 in ref 61.
- (74) See eqs 3.26 and 3.32 in ref 61.
- (75) Kim, Y. C.; Fisher, M. E. *J. Phys. Chem. B* **2001**, *105*, 11785.