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Crossover between vapor-liquid and consolute critical phenomena

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The application of the principle of critical-point universality to fluid mixtures near plait points is generalized to encompass crossover between the one-component vapor-liquid critical limit and the liquid-liquid critical limit of incompressible liquid mixtures. This goal is accomplished by generalizing the scaling fields to linear combinations of three physical field variables related to the temperature and the chemical potentials of the two components. We show how one recovers from the general expressions for the scaling fields the limiting critical behavior of dilute mixtures near the vapor-liquid critical point and of weakly compressible liquid mixtures near the consolute point. In addition we elucidate the consequences for the critical behavior in some special cases, namely, near an azeotropic critical point, near a reentrant critical point, and when the critical temperature goes through a maximum or a minimum as a function of concentration.

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I. INTRODUCTION

Experiments have established that fluids near a critical point belong to the universality class of Ising-like systems [1–3]. The critical behavior in such Ising-like systems is characterized by two relevant scaling fields, a strong ordering field associated with the order-parameter fluctuations and a weak temperaturelike field associated with the energy fluctuations [4]. In a one-component fluid asymptotically close to the vapor-liquid critical point the order parameter and the ordering field may be identified with the density and the chemical potential [3–5].

The concept of critical-point universality can be extended to fluid mixtures provided one selects an appropriate set of thermodynamic variables, two of them playing the role of relevant scaling fields. Specifically, it has been postulated that the thermodynamic behavior of binary fluid mixtures near plait points (i.e., vapor-liquid critical points) is isomorphic with that of near-critical one-component fluids, if the mixtures are not studied at constant composition but with a field variable ζ kept constant [6–8]. Near a critical point the mixtures then satisfy the same universal scaling laws as one-component fluids near the critical point, while the system-dependent amplitudes depend parametrically on the hidden (irrelevant) field ζ. In practice this hidden field ζ has been related to the difference between the chemical potentials of the two components [6,8]. As a consequence, the order-parameter fluctuations are then identified with the density fluctuations at constant ζ [9]. This approach has been used successfully to represent vapor-liquid equilibrium data [10,11] and to develop asymptotic scaled equations of state for such mixtures as He^3+He^4 [12–15], $CO_2+C_2H_4$ [16], $CO_2+C_2H_6$ [17–19], and $CH_4+C_2H_6$ [20]. More recently, the approach has even been extended to deal with the nonasymptotic critical behavior of mixtures including crossover to regular thermodynamic behavior far away from the critical point [21–23].

In the mixtures mentioned above, one is dealing exclusively with vapor-liquid critical phenomena and the vapor-liquid critical line smoothly connects the two critical points of the pure components as schematically indicated in the pressure-temperature diagram shown in Fig. 1. On the other hand, fluid mixtures can exhibit another kind of critical phenomenon, namely, when critical points associated with liquid-liquid equilibria are encountered. The simplest example is the case of two weakly compressible partially miscible liquids that have critical mixing points, also referred to as consolute points [24]. In binary liquid mixtures near a consolute point the order parameter is to be identified with the concentration and the difference between the chemical potentials plays the role of the ordering field conjugate to the order parameter [3]; as we shall see, the role of the hidden field is now played by the chemical potential of one of the components con-

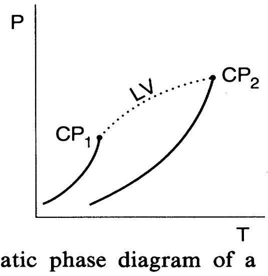

FIG. 1. Schematic phase diagram of a mixture exhibiting type-I phase behavior [25]. The solid curves indicate the vapor-pressure curves of the two pure components. The dotted curve represents the liquid-vapor (LV) critical line of the mixture which connects the two critical points, CP_1 and CP_2, of the pure components (line of plait points).

jugate to the total density. Hence, the ordering field and the hidden field exchange their roles when, in a fluid mixture, the plait point associated with vapor-liquid equilibrium is replaced with the consolute point associated with liquid-liquid equilibrium.

Liquid mixtures are weakly compressible systems and a mixture of two partially miscible incompressible liquids exhibits the limiting behavior of liquid-liquid critical phenomena just as a one-component fluid exhibits the limiting behavior of vapor-liquid critical phenomena in mixtures. These two limits with isolated critical points represent systems with two simple relevant scaling fields.

As elucidated by van Konynenburg and Scott in a systematic fashion, in general one can encounter in fluid mixtures both vapor-liquid and liquid-liquid critical phenomena [25]. In addition to a vapor-liquid critical line between the critical points CP_1 and CP_2 of the two pure components, there may appear a liquid-liquid critical line (line of consolute points) terminating in a critical endpoint CEP as indicated in Fig. 2. An example of a system with this kind of phase behavior, commonly referred to as type-II phase behavior [25,26], is the system carbon dioxide $+n$-octane [27]. More interestingly, the line of plait points, starting at the critical point CP_2 of a pure component, can transform smoothly into a line of consolute points terminating at a critical endpoint CEP_2, where two critical liquid phases and a noncritical vapor phase are in coexistence as indicated in Fig. 3. This behavior has been referred to as type-V phase behavior [25,26] and is, e.g., encountered in mixtures of n-alkanes with appreciable size differences such as methane $+n$-hexane [28]. The line of plait points may also go off into a high-pressure region forming a critical line of gas-gas equilibria as indicated in Fig. 4. An example of a system with such behavior is the mixture neon+xenon [29].

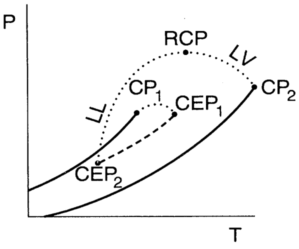

FIG. 3. Schematic phase diagram of a mixture exhibiting type-V phase behavior [25]. The solid curves indicate the vapor-pressure curves of the two pure components. The dotted curves indicate critical lines. The dashed curve between two critical endpoints, CEP_1 and CEP_2, indicates a three-phase line where two liquid phases and a vapor phase are in coexistence.

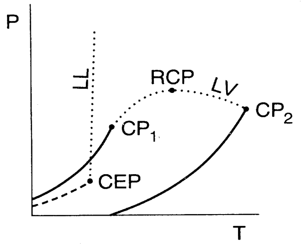

FIG. 2. Schematic phase diagram of a mixture exhibiting type-II phase behavior [25]. The solid curves indicate the vapor-pressure curves of the two pure components. The dotted curves represent liquid-vapor (LV) and liquid-liquid (LL) critical lines. The dashed curve indicates a three-phase line where two liquid phases and a vapor phase are in coexistence terminating in a critical endpoint (CEP). The point at which $dP_c/dT=0$ is sometimes called a reentrant critical point (RCP).

The traditional way of implementing the isomorphism formulation for critical phenomena needs to be generalized when one wants to deal with fluid mixtures that exhibit both vapor-liquid and liquid-liquid critical phenomena. In general one must expect that the ordering field and the hidden field change continuously when the composition varies [30,31]. The difficulty can be illustrated by analyzing the stability criterion for binary mixtures [26]:

$$\left(\frac{\partial^2 A}{\partial x^2}\right)_{V,T}\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,x}-\left(\frac{\partial^2 A}{\partial x\,\partial V}\right)_{T}^{2}\geq 0\,, \tag{1.1}$$

where A and V are the Helmholtz free energy and volume taken per mole, x the mole fraction of component 2, designated as the solute, and T the temperature. At either a vapor-liquid or a liquid-liquid critical point the determinant (1.1) should vanish. Depending on the choice of the density variable associated with the order parameter, the molar density $\rho=V^{-1}$ or the composition x, one can rewrite (1.1) in terms of two different inverse susceptibilities:

$$-\left(\frac{\partial P}{\partial V}\right)_{T,\mu}=-\left(\frac{\partial P}{\partial V}\right)_{T,x}-\frac{(\partial\mu/\partial V)_{T,x}^{2}}{(\partial\mu/\partial x)_{T,V}}\geq 0 \tag{1.2}$$

or

$$\left(\frac{\partial\mu}{\partial x}\right)_{T,P}=\left(\frac{\partial\mu}{\partial x}\right)_{T,V}+\frac{(\partial P/\partial x)_{T,V}^{2}}{(\partial P/\partial V)_{T,x}}\geq 0\,. \tag{1.3}$$

In these equations $\mu=(\partial A/\partial x)_{T,V}=\mu_2-\mu_1$ is the difference between the chemical potentials of the two

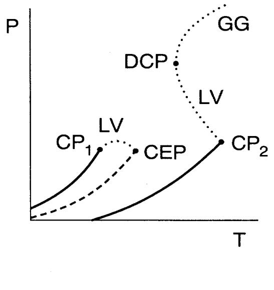

FIG. 4. Schematic phase diagram of a mixture exhibiting type-III phase behavior [25]. The solid curves indicate the vapor-pressure curves of the two pure components. The dotted curves indicate liquid-vapor (LV) and gas-gas (GG) critical lines. The point where the critical line goes through a temperature minimum is called a double critical point (DCP).

components 1 and 2 and $P=-(\partial A/\partial V)_{T,x}$ is the pressure. In applying Eqs. (1.2) and (1.3) it may be noted that

$$\left[\frac{\partial\mu}{\partial V}\right]_{T,x}=-\left[\frac{\partial P}{\partial x}\right]_{T,V} . \tag{1.4}$$

While stability criterion (1.2) is a natural one for plait points as a generalization of a one-component vapor-liquid critical point, $(\partial P/\partial V)_{T,\mu}$ cannot serve as the inverse susceptibility near the consolute point of an incompressible liquid mixture. Similarly, criterion (1.3) will fail in the one-component limit where $(\partial^2 A/\partial V^2)_{T,x}=-(\partial P/\partial V)_{T,x}$ vanishes.

It is the purpose of the present paper to develop a global isomorphism approach for fluid mixtures which encompasses both vapor-liquid critical behavior of one-component fluids and consolute critical behavior of incompressible liquid mixtures as natural limits. This goal will be accomplished by introducing appropriately mixed scaling fields. In this approach the physical intensive variables, such as the temperature and the chemical potentials, do not have a definite scaling dimensionality. Instead, linear combinations of the physical intensive variables will serve as the strong ordering field and the weak scaling field. Thus no individual physical intensive variable will serve as a "hidden" field and no individual physical density variable will serve as a "hidden" variable. All fields and densities enter equally in this global isomorphism formulation and the approach to specific critical-point limits will be controlled by the values of the corresponding coefficients in the linear combinations that serve as the relevant scaling fields.

II. SCALING FIELDS IN A NEAR-CRITICAL ONE-COMPONENT FLUID

Originally, the principle of critical-point universality was developed for systems with an isolated critical point that is characterized by two relevant scaling fields, a strong ordering field h_1 conjugate to the order parameter ϕ_1 and a weak field h_2 [32]. For the Ising model, which has served as the simplest prototype of such a system, the ordering field is the magnetic field and the order parameter is the magnetization [4]. The choice of the corresponding variables for fluids has been guided by the properties of the lattice gas, where the chemical potential difference $g-g_c$ plays the role of the magnetic field and the density difference $\rho-\rho_c$ the role of the magnetization [5,33]. In terms of dimensionless quantities [3]

$$h_1=(g-g_c)/RT_c , \tag{2.1}$$

$$\phi_1=(\rho-\rho_c)/\rho_c , \tag{2.2}$$

where R is the molar gas constant. In this paper we follow the usual convention in which the subscript or superscript c denotes the value of a quantity at the critical point. The weak field h_2 and its corresponding density ϕ_2 are

$$h_2=\tau=(T-T_c)/T_c , \tag{2.3}$$

$$\phi_2=(s-s_c)/R\rho_c , \tag{2.4}$$

where s is the entropy density, i.e., the entropy per unit volume. In recent years it has become evident that in dealing with nonasymptotic critical behavior it is more advantageous to identify the weak field h_2 with $(T-T_c)/T$ rather than with $(T-T_c)/T_c$ [34,35]. The corresponding density ϕ_2 is then to be identified with a difference in the energy density u rather than the entropy density s. However, in the present paper we are concerned with the thermodynamic behavior in the near vicinity of the critical point, where this difference becomes unimportant.

The dependent field variable is the pressure P, which is the density of the thermodynamic potential $\Omega=-PV$. It satisfies the differential relation [5]

$$dP=s\,dT+\rho\,dg . \tag{2.5}$$

To specify the thermodynamic behavior of the fluid near the critical point, the pressure is decomposed as

$$P=\Delta P(h_1,h_2)+P^r(T,g) , \tag{2.6}$$

where $P^r(T,g)$ is a regular background term which is an analytic function of its variables T and g [36,37]. In this paper we use a superscript r to indicate regular contributions to thermodynamic properties. Near the critical point the singular part $\Delta P(h_1,h_2)$ satisfies a scaling law of the form [3,4,38]

$$\Delta P/\rho_c RT_c\equiv\Delta\tilde{P}=h_2^{2-\alpha}f(z) , \tag{2.7}$$

with

$$z=h_1/h_2^{\beta+\gamma} , \tag{2.8}$$

and where $f(z)$ is a universal scaling function. For $h_2<0$, h_2 is to be identified with $|h_2|$ in the scaling laws.

The susceptibility $\chi_1=(\partial\phi_1/\partial h_1)_{h_2}$ exhibits a strong singularity at the critical point. Specifically in the one-phase region in zero field $h_1=0$ the susceptibility diverges as

$$\left[\frac{\partial\phi_1}{\partial h_1}\right]_{h_2}=\Gamma_0 h_2^{-\gamma}=\Gamma_0\tau^{-\gamma} . \tag{2.9}$$

The isochoric molar heat capacity C_V has a weak singularity

$$C_V/R=\left[\frac{\partial\phi_2}{\partial h_2}\right]_{\phi_1}=A_0 h_2^{-\alpha}=A_0\tau^{-\alpha} . \tag{2.10}$$

The order parameter in zero field varies along the two branches of the phase boundary below the critical temperature as

$$\phi_1=\pm B_0|h_2|^{\beta}=\pm B_0|\tau|^{\beta} . \tag{2.11}$$

Here $\alpha=0.110$, $\beta=0.326$, and $\gamma=1.238$ are universal critical exponents, while A_0, B_0, and Γ_0 are system-dependent amplitudes interrelated by the universal amplitude ratio $\alpha A_0\Gamma_0/B_0^2=0.06$ [36,39]. It should be noted that in general the chemical potential at the critical isochore $\rho=\rho_c$ is not a constant but a function of temperature which for the lattice gas is an analytic function

$g_0(T)$. Hence, in practice the ordering field (2.1) is generalized to [5,36]

$$h_1=[g-g_0(T)]/RT_c\ , \tag{2.12}$$

which does not lead to any modification of the thermodynamic behavior near the critical point, since in first approximation the temperature dependence of g does not affect any measurable physical quantity.

The simple Ising model, and consequently the lattice gas, has a special symmetry with respect to the sign of the ordering field h_1. As a result, the density fluctuations and the fluctuations $\delta s=s-\langle s\rangle$ in the entropy density, or equivalently the fluctuations $\delta u=u-\langle u\rangle$ in the energy density, are statistically independent on the critical isochore, i.e., $\langle\delta\rho\,\delta u\rangle=0$. Real fluids, however, do not possess the symmetry of the lattice gas, so that $\langle\delta\rho\,\delta u\rangle\neq0$ [38]. Thus in real fluids the energy fluctuations have a strongly fluctuating component [40]. As a consequence, the chemical potential and temperature themselves have no definite scaling dimensionality and one should identify the scaling fields with the linear combinations [38]

$$h_1=a_1\Delta g+a_2\Delta T\ , \tag{2.13}$$

$$h_2=b_1\Delta T+b_2\Delta g\ , \tag{2.14}$$

where $\Delta g=g-g_c$ and $\Delta T=T-T_c$, while a_i and b_i are system-dependent coefficients to be determined from a comparison with experimental data. These scaling fields are made dimensionless by taking a_1 and b_2 proportional to $1/RT_c$ and a_2 and b_1 proportional to $1/T_c$. In the one-component fluid limit we shall in practice normalize the scaling fields by taking

$$a_1=\frac{1}{RT_c},\quad b_1=\frac{1}{T_c} \tag{2.15}$$

so as to remain consistent with (2.1) and (2.3).

The fact that the weak scaling field h_2 has a component proportional to Δg was originally noticed from an analysis of the decorated lattice gas [41]. On comparing (2.13) with (2.12) we note that the coefficient a_2 is proportional to $-(\partial g/\partial T)_{h_1=0}$. Since g_c and $(\partial g/\partial T)_{h_1=0}$ depend on the choice of zero energy and zero entropy, the coefficient a_2 in (2.13) is arbitrary. Specifically, the values of $(\partial g/\partial T)_P=-S$, where S is the molar entropy, and of $(\partial g/\partial T)_{h_1=0}=-a_2/a_1$ at the critical point depend on the choice of zero point of entropy. With the path $h_1=0$ chosen so as to coincide asymptotically with the critical isochore $\rho=\rho_c$, the difference

$$S_c-a_2/a_1=\rho_c^{-1}(\partial P/\partial T)^c_{h_1=0} \tag{2.16}$$

is well defined at the critical point. The coefficient b_2 in (2.14) is often referred to as the mixing parameter [36,41]; it has an important physical consequence, since it causes a nonclassical behavior of the coexistence-curve diameter as discussed below.

For real fluids the singular part of the field-dependent potential P has the same dependence (2.7) on the fields h_1 and h_2 as that for the lattice gas, but the definition of the scaling field h_2, as given by (2.14), differs from the scaling field h_2 as given by (2.3). We note that the potential $\Delta\tilde{P}$ in (2.7) is a universal function of h_1 and h_2 except for two system-dependent scale factors relating h_1 and h_2 to the physical fields [3,5,36]. In principle, these scale factors are represented by the coefficients a_1 and b_1 in (2.13) and (2.14). If the choice (2.15) is made for a_1 and b_1, then two other scale factors need to be introduced into the scaling function $f(z)$ so as to reproduce the power laws (2.9) and (2.11) with the actual amplitudes Γ_0 and B_0.

The densities conjugate to h_1 and h_2 are

$$\phi_1=\left[\frac{\partial\Delta\tilde{P}}{\partial h_1}\right]_{h_2}=h_2^{\beta}f'(z)$$
$$=\frac{1}{\rho_cRT_c}\left[\frac{b_1}{a_1b_1-a_2b_2}\Delta\rho-\frac{b_2}{a_1b_1-a_2b_2}\Delta s\right]\ , \tag{2.17}$$

$$\phi_2=\left[\frac{\partial\Delta\tilde{P}}{\partial h_2}\right]_{h_1}=h_2^{1-\alpha}\psi(z)$$
$$=\frac{1}{\rho_cRT_c}\left[\frac{a_1}{a_1b_1-a_2b_2}\Delta s-\frac{a_2}{a_1b_1-a_2b_2}\Delta\rho\right]\ , \tag{2.18}$$

where $f'(z)=df/dz$ and

$$\psi(z)=(2-\alpha)f(z)-(\beta+\gamma)zf'(z)\ . \tag{2.19}$$

Hence, the densities ϕ_1 and ϕ_2 conjugate to the scaling fields are linear combinations of the physical densities $\Delta\rho=\rho-\rho_c$ and $\Delta s=s-s_c$. Specifically, the order parameter ϕ_1 is not simply proportional to $\Delta\rho$ but contains a contribution proportional to Δs. As a consequence $\Delta\rho$ along the two branches of the phase boundary varies asymptotically as

$$\Delta\rho/\rho_c=\pm B_0|\tau|^{\beta}+D_0|\tau|^{1-\alpha} \tag{2.20}$$

with

$$B_0=(1-RT_c^2a_2b_2)^{\beta}f'(0) \tag{2.21}$$

and

$$D_0=b_2RT_c(1-RT_c^2a_2b_2)^{1-\alpha}(2-\alpha)f(0)\ . \tag{2.22}$$

The second term in (2.20) causes singular asymptotic behavior of the coexistence-curve diameter [42]. Associated with the densities ϕ_1 and ϕ_2 we may define susceptibilities χ_1 and χ_2:

$$\chi_1=\left(\frac{\partial\phi_1}{\partial h_1}\right)_{h_2}=h_2^{-\gamma}f''(z)\ , \tag{2.23}$$

$$\chi_2=\left(\frac{\partial\phi_2}{\partial h_2}\right)_{h_1}=h_2^{-\alpha}\Psi(z)\ , \tag{2.24}$$

with $\Psi(z)=(1-\alpha)\psi(z)-(\beta+\gamma)z\psi'(z)$ and where $f''(z)=d^2f/dz^2$ and $\psi'(z)=d\psi/dz$. In addition we may define a cross susceptibility as

$$\begin{aligned}\chi_{12}&=\left(\frac{\partial\phi_1}{\partial h_2}\right)_{h_1}\\&=\chi_{21}\\&=\left(\frac{\partial\phi_2}{\partial h_1}\right)_{h_2}\\&=h_2^{\beta-1}[\beta f'(z)-(\beta+\gamma)zf''(z)]\ .\end{aligned} \tag{2.25}$$

For $h_1=0$ and at $h_2>0$ (above the critical point) the order parameter ϕ_1 is zero and χ_{12} vanishes in zero field in the one-phase region. Using (2.17) and (2.18) we obtain for the susceptibilities associated with the physical densities ρ and s:

$$\begin{aligned}\left(\frac{\partial\rho}{\partial g}\right)_T&=\rho\left(\frac{\partial\rho}{\partial P}\right)_T\\&=\rho\left(\frac{\partial\rho}{\partial P}\right)_T^r+\rho_cRT_c(a_1^2\chi_1+b_2^2\chi_2+2a_1b_2\chi_{12})\end{aligned} \tag{2.26}$$

and

$$\left(\frac{\partial s}{\partial T}\right)_g=\left(\frac{\partial s}{\partial T}\right)_g^r+\rho_cRT_c(a_2^2\chi_1+b_1^2\chi_2+2a_2b_1\chi_{12})\ , \tag{2.27}$$

where the superscript r here and hereafter denotes derivatives of the regular part P^r of the pressure in Eq. (2.6).

Using (2.26) and (2.27) we obtain for the isochoric heat capacity per unit volume

$$\rho C_V=T\left(\frac{\partial s}{\partial T}\right)_\rho=T\left(\frac{\partial s}{\partial T}\right)_s-T\left(\frac{\partial g}{\partial T}\right)_\rho^2\left(\frac{\partial \rho}{\partial g}\right)_T\ . \tag{2.28}$$

Since

$$\left(\frac{\partial g}{\partial T}\right)_\rho=-\left(\frac{\partial\rho}{\partial T}\right)_g\left(\frac{\partial g}{\partial\rho}\right)_T \tag{2.29}$$

and

$$\left(\frac{\partial\rho}{\partial T}\right)_g=\left(\frac{\partial\rho}{\partial T}\right)_g^r+\rho_cRT_c(a_1a_2\chi_1+b_1b_2\chi_2)\ , \tag{2.30}$$

the expression for $(\partial g/\partial T)_\rho$ near the critical point becomes

$$\left(\frac{\partial g}{\partial T}\right)_\rho=-\left(\frac{a_1a_2\chi_1+b_1b_2\chi_2}{a_1^2\chi_1+b_2^2\chi_2}\right)\ . \tag{2.31}$$

At the critical point

$$\left(\frac{\partial g}{\partial T}\right)_\rho^c=\left(\frac{\partial g}{\partial T}\right)_{h_1=0}^c=-\frac{a_2}{a_1}\ . \tag{2.32}$$

For the isochoric heat capacity per unit volume in zero field $h_1=0$ in the one-phase region one obtains

$$\begin{aligned}(\rho/\rho_c)(C_V/R)-\frac{T}{\rho_cR}\left(\frac{\partial s}{\partial T}\right)_\rho^r&=\frac{(1-a_2b_2/a_1b_1)^2T_c^2b_1^2\chi_2}{1+(b_2/a_1)^2\chi_2\chi_1^{-1}}\\&=A_0\tau^{-\alpha}+A_1\tau^{\gamma-2\alpha}+\cdots\end{aligned} \tag{2.33}$$

with coefficients [33]

$$A_0=(1-RT_c^2a_2b_2)^{2-\alpha}(2-\alpha)(1-\alpha)f(0) \tag{2.34}$$

and

$$\begin{aligned}A_1=&-(RT_cb_2)^2(1-RT_c^2a_2b_2)^{\gamma-2\alpha+2}(2-\alpha)^2\\&\times(1-\alpha)^2f^2(0)/f''(0)\ .\end{aligned} \tag{2.35}$$

The isothermal compressibility in zero field $h_1=0$ in the one-phase region behaves as

$$RT_c\left(\frac{\partial\rho}{\partial P}\right)_T=RT_c\left(\frac{\partial\rho}{\partial P}\right)_T^r+\Gamma_0\tau^{-\gamma}+\Gamma_1\tau^{-\alpha} \tag{2.36}$$

with

$$\Gamma_0=(1-RT_c^2a_2b_2)^{-\gamma}f''(0) \tag{2.37}$$

and

$$\Gamma_1=(RT_cb_2)^2(1-RT_c^2a_2b_2)^{-\alpha}(2-\alpha)(1-\alpha)f(0)\ . \tag{2.38}$$

It may be interesting to remark that the amplitudes A_0, D_0, A_1, and Γ_1 obey the simple universal relation

$$(1-\alpha)^2D_0^2=A_0\Gamma_1=-A_1\Gamma_0\ . \tag{2.39}$$

It is also worthy to note that the coefficients a_2 and b_2 cannot be determined from any experiment independently. The coefficients a_2 and b_2 enter the critical amplitudes of the asymptotic power laws for physically measurable quantities in such a way that they disappear in any of the universal amplitude ratios such as $A_0\Gamma_0/B_0^2$ and $A_0\Gamma_1/D_0^2$. The mixing of the field variables does not affect the asymptotic critical scaling-law behavior and does not violate the concept of asymptotic critical-point universality. The only effect of the mixing is the appearance of nonasymptotic corrections. However, as we shall elucidate below, in binary mixtures the mixing of field variables has more significant consequences, changing in some cases the asymptotic critical behavior.

III. SCALING FIELDS IN BINARY MIXTURES

In binary mixtures the density $-P=\Omega/V$ of the thermodynamic potential Ω is a function of three field variables, namely, the temperature T, the chemical potential μ_1 of the solvent, and the difference $\mu=\mu_2-\mu_1$ between the chemical potentials μ_1 and μ_2 of the components:

$$dP=s\,dT+\rho\,d\mu_1+\rho_2 d\mu\ , \tag{3.1}$$

where $\rho_2=\rho x$ is the partial density of the solute. Here ρ is the molar density of the mixture and x the mole fraction of the solute. The application of the principle of critical-point universality implies that the thermodynamic behavior of near-critical mixtures is still characterized by two scaling fields h_1 and h_2, so that the scaling law (2.7) remains valid near any critical point [2]. However, these scaling fields are now in general linear combinations of the three physical field variables $\Delta T=T-T_c$, $\Delta\mu_1=\mu_1-\mu_{1c}$, and $\Delta\mu=\mu-\mu_c$:

$$h_1=a_1\Delta\mu_1+a_2\Delta T+a_3\Delta\mu\ , \tag{3.2}$$

$$h_2=b_1\Delta T+b_2\Delta\mu_1+b_3\Delta\mu\ . \tag{3.3}$$

It should be noted that all system-dependent parameters in (3.2) and (3.3), namely, the coefficients a_i and b_i as well as the critical parameters T_c, μ_{1c}, and μ_c, depend parametrically on the actual position on the critical line. This position can be specified by any of the three variables T_c, μ_{1c}, or μ_c. An important difference between the definitions of h_1 and h_2 for mixtures as compared to those for one-component fluids is that all coefficients a_i and b_i are system-dependent functions of the position on the critical line. A representation of the two scaling fields h_1 and h_2 for binary mixtures in the form of a linear combination of the three physical field variables was first proposed by Saam [7], who, however, considered vapor-liquid critical phenomena only.

The pressure P can again be separated into a singular and a regular part,

$$P=\Delta P(h_1,h_2)+P^r(T,\mu_1,\mu)\ , \tag{3.4}$$

where the regular part P^r is now an analytic function of the three field variables T, μ_1, and μ. The singular part ΔP satisfies a scaling law analogous to (2.7):

$$\Delta P/\rho_c^0 R T_c^0=\Delta\tilde{P}=h_2^{2-\alpha}f(z)\ , \tag{3.5}$$

where ρ_c^0 and T_c^0 are the critical density and the critical temperature of the pure solvent. Noting that $\rho=(\partial P/\partial\mu_1)_{T,\mu}$, $s=(\partial P/\partial T)_{\mu_1,\mu}$, and $\rho_2=(\partial P/\partial\mu)_{T,\mu_1}$ and retaining the definitions $\phi_1=(\partial\Delta\tilde{P}/\partial h_1)_{h_2}$ and $\phi_2=(\partial\Delta\tilde{P}/\partial h_2)_{h_1}$, we obtain

$$\Delta\rho=\rho-\left[\frac{\partial P^r}{\partial\mu_1}\right]_{\mu,T}=(a_1\phi_1+b_2\phi_2)\rho_c^0 R T_c^0\ , \tag{3.6}$$

$$\Delta\rho_2=\rho_2-\left[\frac{\partial P^r}{\partial\mu}\right]_{\mu_1,T}=(a_3\phi_1+b_3\phi_2)\rho_c^0 R T_c^0\ , \tag{3.7}$$

$$\Delta s=s-\left[\frac{\partial P^r}{\partial T}\right]_{\mu,\mu_1}=(a_2\phi_1+b_1\phi_2)\rho_c^0 R T_c^0\ . \tag{3.8}$$

In first approximation $\Delta\rho=\rho-\rho_c$, $\Delta\rho_2=\rho_2-\rho_{2c}$, and $\Delta s=s-s_c$. Thus the relevant densities ϕ_1 and ϕ_2 can be expressed as linear combinations of any two of the three physical densities $\Delta\rho$, $\Delta\rho_2$, and Δs:

$$\phi_1=\frac{1}{\rho_c^0 R T_c^0}\left[\frac{b_1}{a_1b_1-a_2b_2}\Delta\rho-\frac{b_2}{a_1b_1-a_2b_2}\Delta s\right]\ , \tag{3.9}$$

$$\phi_1=\frac{1}{\rho_c^0 R T_c^0}\left[\frac{b_2}{a_3b_2-a_1b_3}\Delta\rho_2-\frac{b_3}{a_3b_2-a_1b_3}\Delta\rho\right]\ , \tag{3.10}$$

$$\phi_1=\frac{1}{\rho_c^0 R T_c^0}\left[\frac{b_3}{a_2b_3-a_3b_1}\Delta s-\frac{b_1}{a_2b_3-a_3b_1}\Delta\rho_2\right]\ , \tag{3.11}$$

$$\phi_2=\frac{1}{\rho_c^0 R T_c^0}\left[\frac{a_1}{a_1b_1-a_2b_2}\Delta s-\frac{a_2}{a_1b_1-a_2b_2}\Delta\rho\right]\ , \tag{3.12}$$

$$\phi_2=\frac{1}{\rho_c^0 R T_c^0}\left[\frac{a_2}{a_2b_3-a_3b_1}\Delta\rho_2-\frac{a_3}{a_2b_3-a_3b_1}\Delta s\right]\ , \tag{3.13}$$

$$\phi_2=\frac{1}{\rho_c^0 R T_c^0}\left[\frac{a_3}{a_3b_2-a_1b_3}\Delta\rho-\frac{a_1}{a_3b_2-a_1b_3}\Delta\rho_2\right]\ . \tag{3.14}$$

The susceptibilities χ_1 and χ_2 and χ_{12} are again given by Eqs. (2.23)–(2.25). Using (3.6) and (3.7) we obtain for the response functions associated with the physical densities ρ and ρ_2:

$$\begin{aligned}\left[\frac{\partial\rho}{\partial\mu_1}\right]_{\mu,T}&=\rho\left[\frac{\partial\rho}{\partial P}\right]_{\mu,T}\\&=\rho\left[\frac{\partial\rho}{\partial P}\right]_{\mu,T}^{r}\\&\quad+\rho_c^0 R T_c^0(a_1^2\chi_1+b_2^2\chi_2+2a_1b_2\chi_{12})\end{aligned} \tag{3.15}$$

in analogy with Eq. (2.26), and

$$\begin{aligned}\left[\frac{\partial\rho_2}{\partial\mu}\right]_{P,T}&=\rho\left[\frac{\partial x}{\partial\mu}\right]_{P,T}+x\left[\frac{\partial\rho}{\partial\mu}\right]_{P,T}\\&=\left[\frac{\partial\rho_2}{\partial\mu}\right]_{P,T}^{r}+\rho_c^0 R T_c^0\{a_3(a_3-a_1x)\chi_1+b_3(b_3-b_2x)\chi_2+[b_3(2a_3-a_1x)-a_3b_2x]\chi_{12}\}\ .\end{aligned} \tag{3.16}$$

In practice one does not measure experimentally $(\partial\rho_2/\partial\mu)_{P,T}$ but rather the osmotic compressibility $(\partial x/\partial\mu)_{P,T}$, which is directly related to the diffusion coefficient [3] and which near the consolute point is proportional to the intensity of scattered light [43]. To obtain the latter quantity from (3.16) we note that

$$\left[\frac{\partial\rho}{\partial\mu}\right]_{P,T}=\left[\frac{\partial\rho}{\partial\mu}\right]_{\mu_1,T}-\rho x\left[\frac{\partial\rho}{\partial P}\right]_{\mu,T} \tag{3.17}$$

with

$$\left[\frac{\partial\rho}{\partial\mu}\right]_{\mu_1,T}=\left[\frac{\partial\rho}{\partial\mu}\right]^r_{\mu_1,T}+\rho_c^0RT_c^0[a_1a_3\chi_1+b_2b_3\chi_2+(a_1b_3+a_3b_2)\chi_{12}]\ . \tag{3.18}$$

From (3.16)–(3.18) we thus obtain

$$\rho\left[\frac{\partial x}{\partial\mu}\right]_{P,T}=\rho\left[\frac{\partial x}{\partial\mu}\right]^r_{P,T}+\rho_c^0RT_c^0[(a_3-a_1x)^2\chi_1+(b_3-b_2x)^2\chi_2+2\{a_3b_3-(a_1b_3+a_3b_2)x+a_1b_2x^2\}\chi_{12}]\ . \tag{3.19}$$

At $h_1=0$ and $h_2>0$, $\phi_1=0$, so that the cross susceptibility χ_{12} in the equations above vanishes in zero ordering field in the one-phase region.

Other measurable quantities are $(\partial\rho/\partial P)_{T,x}$, associated with the coefficient of the isothermal compressibility, and the isochoric and isobaric heat capacities per unit volume at constant composition $\rho C_{V,x}$ and $\rho C_{P,x}$:

$$\left[\frac{\partial\rho}{\partial P}\right]_{T,x}=\left[\frac{\partial\rho}{\partial P}\right]_{T,\mu}-\frac{1}{\rho^2}\left[\frac{\partial\rho}{\partial\mu}\right]^2_{P,T}\left[\frac{\partial\mu}{\partial x}\right]_{P,T}, \tag{3.20}$$

$$\rho C_{V,x}=T\left[\frac{\partial s}{\partial T}\right]_{\rho,\mu}-T\left[\frac{\partial\mu}{\partial T}\right]^2_{\rho,x}\left[\frac{\partial x}{\partial\mu}\right]_{\rho,T}, \tag{3.21}$$

$$\rho C_{P,x}=\rho C_{V,x}+\frac{T}{\rho}\left[\frac{\partial P}{\partial T}\right]^2_{\rho,x}\left[\frac{\partial\rho}{\partial P}\right]_{T,x}\ . \tag{3.22}$$

From Eqs. (3.15), (3.17), and (3.20) we have in zero field in the one-phase region ($\chi_{12}=0$):

$$\begin{aligned}\left[\frac{\partial\rho}{\partial P}\right]_{T,x}&\\
=\left[\frac{\partial\rho}{\partial P}\right]^r_{T,x}&\\
+\frac{a_1^2\chi_1\left\{\left[\dfrac{\rho_c^0RT_c^0}{\rho_c}\right]^2\left[\left[\dfrac{\partial x}{\partial\mu}\right]^r_{P,T}\right]^{-1}K_2^2\chi_2+\left[1+\dfrac{1}{\rho_c}\left[\dfrac{\partial\rho}{\partial x}\right]^r_{P,T}K_1\right]^2+\left[\dfrac{b_2}{a_1}-\dfrac{1}{\rho_c}\left[\dfrac{\partial\rho}{\partial x}\right]^r_{P,T}\left[\dfrac{b_3-b_2x}{a_1}\right]\right]^2\chi_2\chi_1^{-1}\right\}}{1+\dfrac{\rho_c^0RT_c^0}{\rho_c}\left[\left[\dfrac{\partial x}{\partial\mu}\right]^r_{P,T}\right]^{-1}[a_1^2K_1^2\chi_1+(b_3-b_2x)^2\chi_2]}&,\end{aligned} \tag{3.23}$$

where we have introduced quantities K_1 and K_2 defined as

$$K_1=-\left[\frac{a_3}{a_1}-x\right] \tag{3.24}$$

and

$$K_2=\left[\frac{b_2}{a_1}(a_3-a_1x)-(b_3-b_2x)\right]=a_3b_2/a_1-b_3\ . \tag{3.25}$$

Expression (3.21) for the isochoric molar heat capacity contains two quantities which are generally weakly divergent and generally compensate each other at the critical point of a mixture:

$$\left[\frac{\partial s}{\partial T}\right]_{\rho,\mu}=\left[\frac{\partial s}{\partial T}\right]_{\mu,\mu_1}-\left[\frac{\partial\rho}{\partial T}\right]^2_{\mu,\mu_1}\left[\frac{\partial\mu_1}{\partial\rho}\right]_{T,\mu}, \tag{3.26}$$

$$\left[\frac{\partial x}{\partial \mu}\right]_{\rho,T}=\left[\frac{\partial x}{\partial \mu}\right]_{P,T}-\frac{1}{\rho^2}\left[\frac{\partial \rho}{\partial \mu}\right]_{P,T}^{2}\left[\frac{\partial P}{\partial \rho}\right]_{\mu,T} . \tag{3.27}$$

From Eqs. (3.6) and (3.8) we have

$$\left[\frac{\partial \rho}{\partial T}\right]_{\mu,\mu_1}=\left[\frac{\partial \rho}{\partial T}\right]_{\mu,\mu_1}^{r}+\rho_c^0RT_c^0(a_1a_2\chi_1+b_1b_2\chi_2) , \tag{3.28}$$

$$\left[\frac{\partial s}{\partial T}\right]_{\mu,\mu_1}=\left[\frac{\partial s}{\partial T}\right]_{\mu,\mu_1}^{r}+\rho_c^0RT_c^0(a_2^2\chi_1+b_1^2\chi_2) . \tag{3.29}$$

Substituting (3.28) and (3.29) into (3.26), and (3.15), (3.17), and (3.19) into (3.27), respectively, we finally obtain in zero field in the one-phase region

$$\left[\frac{\partial s}{\partial T}\right]_{\rho,\mu}=\left[\frac{\partial s}{\partial T}\right]_{\rho,\mu}^{r}+\frac{\rho_c^0RT_c^0\chi_1\left\{\dfrac{\rho_c^0RT_c^0}{\rho_c}\left[\left[\dfrac{\partial \rho}{\partial P}\right]_{\mu,T}^{r}\right]^{-1}(a_1b_1-a_2b_2)^2\chi_2+\left[a_1\left[\dfrac{\partial \mu_1}{\partial T}\right]_{\rho,\mu}^{r}+a_2\right]^2+\left[b_2\left[\dfrac{\partial \mu_1}{\partial T}\right]_{\rho,\mu}^{r}+b_1\right]^2\chi_2\chi_1^{-1}\right\}}{1+\dfrac{\rho_c^0RT_c^0}{\rho_c}\left[\left[\dfrac{\partial \rho}{\partial P}\right]_{\mu,T}^{r}\right]^{-1}(a_1^2\chi_1+b_2^2\chi_2)} \tag{3.30}$$

and

$$\left[\frac{\partial x}{\partial \mu}\right]_{\rho,T}=\left[\frac{\partial x}{\partial \mu}\right]_{\rho,T}^{r}+\frac{a_1^2\chi_1\left\{\left[\dfrac{\rho_c^0RT_c^0}{\rho_c}\right]^2\left[\left[\dfrac{\partial \rho}{\partial P}\right]_{\mu,T}^{r}\right]^{-1}K_2^2\chi_2+\left[\rho_c\left[\dfrac{\partial x}{\partial \rho}\right]_{\mu,T}^{r}+K_1\right]^2+\left[\rho_c\left[\dfrac{\partial x}{\partial \rho}\right]_{\mu,T}^{r}\dfrac{b_2}{a_1}-\left[\dfrac{b_3-b_2x}{a_1}\right]\right]^2\chi_2\chi_1^{-1}\right\}}{1+\dfrac{\rho_c^0RT_c^0}{\rho_c}\left[\left[\dfrac{\partial \rho}{\partial P}\right]_{\mu,T}^{r}\right]^{-1}(a_1^2\chi_1+b_2^2\chi_2)} . \tag{3.31}$$

From the expressions presented above one can see that all second derivatives of the thermodynamic potential are in general combinations of the strong and weak susceptibilities, χ_1 and χ_2, as is the case for one-component fluids. While for one-component fluids only one of these susceptibilities dominates the near-critical behavior, for mixtures the relative contributions from χ_1 and χ_2 depend on the values of the coefficients a_i and b_i as they vary along the critical line.

IV. ONE-COMPONENT LIMIT

We first consider the behavior of the scaling fields (3.2) and (3.3) in the one-component limit $x \rightarrow 0$. For a dilute solution it is convenient to treat μ as a hidden field [3]. Then

$$h_1=a_1(\mu)\Delta\mu_1(\mu)+a_2(\mu)\Delta T(\mu) , \tag{4.1}$$

$$h_2=b_1(\mu)\Delta T(\mu)+b_2(\mu)\Delta\mu_1(\mu) , \tag{4.2}$$

where all system-dependent parameters depend parametrically on the hidden field μ. Specifically, $\Delta\mu_1(\mu)=\mu_1-\mu_{1c}(\mu)$ and $\Delta T(\mu)=T-T_c(\mu)$. On the critical line we have $\mu_1=\mu_{1c}(\mu)$ and $T=T_c(\mu)$ and the scaling fields h_1 and h_2 vanish. Now we consider the scaling fields h_1 and h_2 at a state where $\mu=\mu_c+\Delta\mu$, $\Delta\mu_1=\mu_1-\mu_{1c}(\mu_c+\Delta\mu)$, and $\Delta T=T-T_c(\mu_c+\Delta\mu)$ near an arbitrary point μ_c on the critical line. Expanding around $\mu=\mu_c$ we obtain in first approximation

$$h_1=a_1(\mu_c)\Delta\mu_1(\mu_c)+a_2(\mu_c)\Delta T(\mu_c)+a_3(\mu_c)\Delta\mu , \tag{4.3}$$

$$h_2=b_1(\mu_c)\Delta T(\mu_c)+b_2(\mu_c)\Delta\mu_1(\mu_c)+b_3(\mu_c)\Delta\mu , \tag{4.4}$$

with

$$a_3 = -\left[a_1 \frac{d\mu_{1c}}{d\mu} + a_2 \frac{dT_c}{d\mu} \right] , \tag{4.5}$$

$$b_3 = -\left[b_1 \frac{dT_c}{d\mu} + b_2 \frac{d\mu_{1c}}{d\mu} \right] . \tag{4.6}$$

In a dilute solution [3]

$$\frac{dT_c}{d\mu} = \frac{dT_c}{dx} \left[\frac{d\mu_c}{dx} \right]^{-1} = \frac{dT_c}{dx} \frac{x}{RT_c} , \tag{4.7}$$

$$\frac{d\mu_{1c}}{d\mu} = \frac{d\mu_{1c}}{dx} \left[\frac{d\mu_c}{dx} \right]^{-1} = \frac{d\mu_{1c}}{dx} \frac{x}{RT_c} . \tag{4.8}$$

We note that in this paper total derivatives are always taken along the critical line.

From (4.7) and (4.8) we conclude that both $dT_c/d\mu$ and $d\mu_{1c}/d\mu$, and thus a_3 and b_3, vanish in the limit $x \to 0$. Thus the general expressions (3.2) and (3.3) reduce to the expressions (2.13) and (2.14) for the one-component solvent with $\mu_1 = g$. Obviously, the expressions (3.9) and (3.12) for ϕ_1 and ϕ_2 become identical to the corresponding expressions (2.17) and (2.18) for the pure solvent. The expressions (3.10) and (3.11) for ϕ_1 and the expressions (3.13) and (3.14) for ϕ_2 of dilute solutions become also identical to (3.9) and (3.12), respectively.

Since the coefficients a_1 and b_2 approach their values for the pure solvent, we note from (3.15) and (2.26) that the response function $(\partial\Delta\rho/\partial\mu_1)_{\mu,T} = \rho(\partial\rho/\partial P)_{\mu,T}$ will behave like the response function $(\partial\Delta\rho/\partial g)_T = \rho(\partial\rho/\partial P)_T$ of the one-component fluid. On the other hand, both the singular part and the regular part of the osmotic compressibility $(\partial x/\partial\mu)_{P,T}$ vanish as $x \to 0$. The singular part vanishes, since in (3.19) both a_3 and b_3 become proportional to x in accordance with (4.5)–(4.8), while the regular part in the dilute solution limit becomes [3]

$$\left[\frac{\partial x}{\partial\mu} \right]_{P,T}^{r} = \left[\frac{\partial x}{\partial\mu} \right]_{\rho,T}^{r} = \frac{x}{RT_c} . \tag{4.9}$$

Since in the one-component limit $a_1 = 1/RT_c^0$ in accordance with (2.15), the expressions for the osmotic compressibility and the isothermal compressibility reduce to

$$\left[\frac{\partial x}{\partial\mu} \right]_{P,T} = \frac{x}{RT_c^0} (1 + x^{-1} K_1^2 \chi_1) , \tag{4.10}$$

$$\left[\frac{\partial\rho}{\partial P} \right]_{T,x} = \left[\frac{\partial\rho}{\partial P} \right]_{T,x}^{r} + \frac{\chi_1}{RT_c^0} \left[\frac{x^{-1}(RT_c^0 K_2)^2 \chi_2 + 1}{1 + x^{-1} K_1^2 \chi_1} \right] . \tag{4.11}$$

For dilute mixtures we can consider two characteristic temperatures τ_1 and τ_2 [3]. The first is defined as the temperature at which the contribution from the singular part of $(\partial x/\partial\mu)_{P,T}$ is comparable to that from the regular part of $(\partial x/\partial\mu)_{P,T}$, so that

$$K_1^2 \chi_1 \simeq 1 . \tag{4.12}$$

Furthermore, it follows from (4.5) and (2.16) that in a dilute solution

$$a_3 = -\frac{x}{\rho_c^0 (RT_c^0)^2} \left[\frac{dP_c}{dx} - \rho_c \left[S_c - \frac{a_2}{a_1} \right] \frac{dT_c}{dx} \right] + \frac{x}{RT_c^0} \tag{4.13}$$

and

$$K_1 = \frac{x}{\rho_c^0 RT_c^0} \left[\frac{dP_c}{dx} - \left[\frac{\partial P}{\partial T} \right]_{\mu=\mu_c, h_1=0}^{c} \frac{dT_c}{dx} \right] . \tag{4.14}$$

The expression in square brackets in Eq. (4.14) has been designated by Levelt Sengers as the Krichevskii parameter [44]. Here $(\partial P/\partial T)_{\mu=\mu_c,h_1=0}^{c}$ denotes the limiting value of $(\partial P/\partial T)_{\mu=\mu_c,h_1=0}$ at the critical point. In a dilute solution the derivative $(\partial P/\partial T)_{\mu=\mu_c,h_1=0}^{c}$ may be identified with $(\partial P/\partial T)_{\rho=\rho_c}^{c}$ at the critical point of the solvent. A characteristic temperature τ_1 may now be defined as

$$\tau_1 \approx X_\Gamma^{1/\gamma} \tag{4.15}$$

with

$$X_\Gamma = \frac{\Gamma_0 x}{(\rho_c^0 RT_c^0)^2} \left[\frac{dP_c}{dx} - \left[\frac{\partial P}{\partial T} \right]_{\mu=\mu_c, h_1=0}^{c} \frac{dT_c}{dx} \right]^2 . \tag{4.16}$$

and where Γ_0 is the amplitude of the asymptotic power law $\chi_1 = \Gamma_0 \tau^{-\gamma}$ for the susceptibility in the one-phase region in zero field. Alternatively, the characteristic temperature τ_1 can be associated with the behavior of $(\partial\rho/\partial P)_{T,x}$ as given by (4.11). For $\tau \gg \tau_1$ $(\partial\rho/\partial P)_{T,x}$ diverges strongly just like the compressibility of one-component fluids. If we do not restrict ourselves to the dilute-solution limit, the quantity X_Γ in the definition (4.15) of the crossover temperature τ_1 can be generalized to

$$X_\Gamma = \frac{\Gamma_0}{RT_c^0} \left[\left[\frac{\partial x}{\partial\mu} \right]_{P,T}^{r} \right]^{-1} K_1^2 , \tag{4.17}$$

with

$$K_1 = \frac{1}{\rho_c} \left[\frac{d\mu_c}{dx} \right]^{-1} \left[\frac{dP_c}{dx} - \left[\frac{\partial P}{\partial T} \right]_{\mu=\mu_c, h_1=0}^{c} \frac{dT_c}{dx} \right] . \tag{4.18}$$

A second characteristic temperature τ_2 may be defined as the temperature where

$$\frac{(RT_c^0)^2}{x} K_2^2 \chi_2 \simeq 1 . \tag{4.19}$$

Since for a dilute solution Eq. (3.25) reduces to

$$K_2 = \frac{1}{T_c^0} \frac{dT_c}{d\mu} = \frac{x}{R(T_c^0)^2} \frac{dT_c}{dx} , \tag{4.20}$$

we obtain

$$\tau_2 \approx X_A^{1/\alpha} \tag{4.21}$$

with

$$X_A = A_0 \frac{(RT_c^0 K_2)^2}{x} = A_0 \frac{x}{(T_c^0)^2} \left[\frac{dT_c}{dx} \right]^2 , \tag{4.22}$$

where A_0 is the amplitude (2.31) in the asymptotic power law $\chi_2 = A_0 \tau^{-\alpha}$ for the weak susceptibility. More generally

$$X_A = \frac{\rho_c^0 R T_c^0}{\rho_c} A_0 \left[\left[\frac{\partial x}{\partial \mu} \right]_{P,T}^{r} \right]^{-1} K_2^2 . \tag{4.23}$$

For $\tau \gg \tau_1$ the compressibility $(\partial \rho / \partial P)_{T,x}$ diverges strongly as mentioned earlier, for $\tau \ll \tau_2$ $(\partial \rho / \partial P)_{T,x}$ diverges weakly as χ_2, while in the intermediate range $\tau_1 < \tau < \tau_2$ $(\partial \rho / \partial P)_{T,x}$ exhibits crossover from strongly divergent to weakly divergent behavior. For $\tau \ll \tau_2$, where $(\partial P / \partial T)_{T,x}$ diverges weakly, $C_{P,x}$ diverges weakly also, while $C_{V,x}$ tends to a finite value. The characteristic temperature τ_2 also determines the so-called Fisher renormalization of critical exponents [45]. Physical quantities measured as a function of temperature at constant composition and constant density will satisfy for $\tau \ll \tau_2$ the asymptotic power laws but with renormalized critical-exponent values [3,4,45].

Thus far we have considered in this section the one-component limit $x \to 0$ corresponding to that of the pure solvent. In addition one can consider the one-component limit $x \to 1$ corresponding to that of the pure solute. For this limit it is convenient to rewrite Eq. (3.2) in the form

$$h_1 = a_1 \Delta\mu_2 + a_2 \Delta T + (a_3 - a_1) \Delta\mu . \tag{4.24}$$

As

$$\lim_{x \to 1} (d\mu_c / dx)^{-1} = \lim_{x \to 1} (1 - x) / RT_c = 0 ,$$

we have from Eqs. (3.24) and (4.18)

$$\frac{a_3}{a_1} = x - K_1 \to 1 , \tag{4.25}$$

and the difference $a_3 - a_1 = -a_1(1 - x + K_1)$ vanishes in the limit of the pure solute. This difference $a_3 - a_1$ plays in the pure-solute limit the same role as a_3 plays in the pure-solvent limit. Meanwhile the difference $a_3 - a_1 x$ behaves symmetrically in both limits.

V. LIMIT OF AN INCOMPRESSIBLE LIQUID MIXTURE

The compressibility of liquids near a consolute point is usually very small. Hence, we consider the limit of critical phase separation in an incompressible liquid mixture. For this purpose we note that on the critical line

$$\frac{dT_c}{d\mu_1} = \frac{dT_c}{dP} \frac{dP_c}{d\mu_1} , \tag{5.1}$$

$$\frac{dx_c}{d\mu_1} = \frac{dx_c}{dP} \frac{dP_c}{d\mu_1} , \tag{5.2}$$

where $dP_c / d\mu_1 \simeq \rho_c$ is finite. Near the incompressible limit the critical parameters T_c and x_c become insensitive to changes in pressure and, hence, insensitive to changes in μ_1. When the compressibility is small, but finite, we treat μ_1 as the hidden field, so that

$$h_1 = a_2(\mu_1) \Delta T(\mu_1) + a_3(\mu_1) \Delta\mu(\mu_1) , \tag{5.3}$$

$$h_2 = b_1(\mu_1) \Delta T(\mu_1) + b_3(\mu_1) \Delta\mu(\mu_1) , \tag{5.4}$$

where $\Delta T(\mu_1) = T - T_c(\mu_1)$ and $\Delta\mu(\mu_1) = \mu - \mu_c(\mu_1)$. We consider the scaling fields h_1 and h_2 in a state where $\mu_1 = \mu_{1c} + \Delta\mu_1$, $\Delta T = T - T_c(\mu_{1c} + \Delta\mu_1)$, and $\Delta\mu = \mu - \mu_c(\mu_{1c} + \Delta\mu_1)$ near an arbitrary point μ_{1c} on the critical line. We then obtain in first approximation in analogy to (4.3) and (4.4):

$$h_1 = a_2(\mu_{1c}) \Delta T(\mu_{1c}) + a_3(\mu_{1c}) \Delta\mu(\mu_{1c}) + a_1(\mu_{1c}) \Delta\mu_1 , \tag{5.5}$$

with

$$h_2 = b_1(\mu_{1c}) \Delta T(\mu_{1c}) + b_3(\mu_{1c}) \Delta\mu(\mu_{1c}) + b_2(\mu_{1c}) \Delta\mu_1 , \tag{5.6}$$

with

$$a_1 = - \left[a_3 \frac{d\mu_c}{d\mu_1} + a_2 \frac{dT_c}{d\mu_1} \right] , \tag{5.7}$$

$$b_2 = - \left[b_3 \frac{d\mu_c}{d\mu_1} + b_1 \frac{dT_c}{d\mu_1} \right] . \tag{5.8}$$

In the incompressible limit $dT_c / d\mu_1 = 0$ and $d\mu_c / d\mu_1 = (d\mu_c / dx)(dx / dP) = 0$ and the coefficients a_1 and b_2 vanish. Thus the general expressions (3.2) and (3.3) for the scaling fields now reduce to

$$h_1 = a_2 \Delta T + a_3 \Delta\mu , \tag{5.9}$$

$$h_2 = b_1 \Delta T + b_3 \Delta\mu . \tag{5.10}$$

On comparing (5.9) and (5.10) with (2.13) and (2.14) we conclude that the thermodynamic behavior near the consolute point in an incompressible liquid mixture is isomorphic with that of a one-component fluid near the vapor-liquid critical point provided that the chemical potential g is replaced with the chemical potential difference $\mu = \mu_2 - \mu_1$. Specifically, the order parameter ϕ_1 is now to be identified with expression (3.11). Using techniques similar to those employed for a dilute solution near the solvent critical point, one can show that the expressions (3.9) and (3.10) for ϕ_1 transform into (3.11) in this liquid-liquid mixture limit. On comparing (5.9) and (5.10) with (2.13) and (2.14) we note that the natural way of normalizing the scaling fields h_1 and h_2 in this limit is to take

$$a_3 = \frac{1}{RT_c} , \quad b_1 = \frac{1}{T_c} . \tag{5.11}$$

In analogy to (2.20) $\Delta\rho_2$ at the phase boundary near the consolute point now exhibits a singular coexistence-curve diameter:

$$\Delta\rho_2 / \rho_{2c} = \pm B_0 |\tau|^{\beta} + D_0 |\tau|^{1-\alpha} \tag{5.12}$$

with

$$B_0=\frac{\rho_c^0T_c^0}{\rho_{2c}T_c}(1-RT_c^2b_3a_2)^{\beta}f'(0) \tag{5.13}$$

and

$$D_0=\frac{\rho_c^0RT_c}{\rho_{2c}}b_3(1-RT_c^2b_3a_2)^{1-\alpha}(2-\alpha)f(0)\ . \tag{5.14}$$

Since upon substituting (5.11) into (5.9) and (5.10)

$$h_1=\frac{\Delta\mu}{RT_c}+a_2\Delta T\ , \tag{5.15}$$

$$h_2=\frac{\Delta T}{T_c}+b_3\Delta\mu\ , \tag{5.16}$$

we have for the strong susceptibility in zero field

$$RT_c\left[\frac{\partial x}{\partial\mu}\right]_{P,T}=RT_c\left[\frac{\partial x}{\partial\mu}\right]_{\rho,T}=\Gamma_0\tau^{-\gamma}+\Gamma_1\tau^{-\alpha}+\cdots \tag{5.17}$$

with

$$\Gamma_0=(1-RT_c^2a_2b_3)^{-\gamma}f''(0) \tag{5.18}$$

and

$$\Gamma_1=(RT_cb_3)^2(1-RT_c^2a_2b_3)^{-\alpha}(2-\alpha)(1-\alpha)f(0) \tag{5.19}$$

to be compared with (2.36). For the molar heat capacity

$$C_{P,x}/R=C_{\rho,x}/R=A_0\tau^{-\alpha}+A_1\tau^{\gamma-2\alpha}+\cdots \tag{5.20}$$

with

$$A_0=(1-RT_c^2a_2b_3)^{2-\alpha}(2-\alpha)(1-\alpha)f(0) \tag{5.21}$$

and

$$A_1=-(RT_cb_3)^2(1-RT_c^2a_2b_3)^{\gamma-2\alpha+2}\times(2-\alpha)^2(1-\alpha)^2f^2(0)/f''(0)\ . \tag{5.22}$$

In real liquid mixtures the compressibility is small but not negligible. We can analyze the behavior of the compressibility $(\partial\rho/\partial\mu_1)_{T,\mu}=\rho(\partial\rho/\partial P)_{T,\mu}$ of a weakly compressible liquid mixture in a manner analogous to the analysis of the osmotic compressibility of a solution near the one-component limit in the preceding section. From (3.15) we estimate that the singular part of the compressibility becomes comparable to its regular part when

$$a_1^2\chi_1\simeq\frac{\rho_c}{\rho_c^0RT_c^0}\left[\frac{\partial\rho}{\partial P}\right]_{T,\mu}^r\ . \tag{5.23}$$

A description of the thermodynamic properties of mixtures is considerably simplified if one uses an approximation, referred to as the critical-line condition [9], which amounts to special choices for the energy or entropy along the critical line. Here we find it convenient to introduce a critical-line condition in the form $a_2=0$, which according to (2.16) implies $S_c=\rho_c^{-1}(\partial P/\partial T)^c_{\mu=\mu_c,h_1=0}$. From (5.7) we then obtain

$$a_1=-a_3\frac{d\mu_c}{dx}\frac{dx_c}{d\mu_1}=-\frac{a_3}{K_1-x}\ , \tag{5.24}$$

where K_1 is again related to the Krichevskii parameter in accordance with Eq. (4.14) and which becomes infinite in the incompressible liquid-mixture limit. Assuming that $K_1\gg x$ in (5.24) and taking $a_3=1/RT_c$ in accordance with (5.11), we now define a characteristic temperature as

$$\tilde{\tau}_1\simeq\tilde{X}_\Gamma^{1/\gamma} \tag{5.25}$$

with

$$\tilde{X}_\Gamma=\frac{\rho_c^0T_c^0\Gamma_0}{\rho_cRT_c^2}\left[\left[\frac{\partial\rho}{\partial P}\right]_{T,\mu}^r\right]^{-1}K_1^{-2}\ . \tag{5.26}$$

For $\tau\ll\tilde{\tau}_1$ the compressibility at constant μ will exhibit a strongly divergent behavior, while for $\tau\gg\tilde{\tau}_1$ the compressibility will behave regularly like that of an ordinary weakly compressible liquid mixture. An order-of-magnitude estimate of $\tilde{X}_\Gamma$ may be obtained by taking $(\partial P/\partial\rho)^r_{T,\mu}\simeq(\partial P/\partial\rho)^r_{T,x}$ and $d\mu_c/dx\simeq RT_c/x(1-x)$. It is interesting to note that the crossover temperature τ_1 defined by (4.15) for a dilute solution is proportional to $K_1^{2/\gamma}$, while the crossover temperature $\tilde{\tau}_1$ defined by (5.25) is inversely proportional to $K_1^{2/\gamma}$.

A second characteristic temperature $\tilde{\tau}_2$ can be deduced from (3.23) as the temperature at which

$$\left[\frac{\partial\rho}{\partial P}\right]_{T,x}^r\simeq RT_c^0\left[\frac{K_2}{K_1}\right]^2\chi_2\ . \tag{5.27}$$

Thus

$$\tilde{\tau}_2\simeq\tilde{X}_A^{1/\alpha} \tag{5.28}$$

with

$$\begin{aligned}\tilde{X}_A&=A_0RT_c^0\left[\left[\frac{\partial\rho}{\partial P}\right]_{T,x}^r\right]^{-1}\left[\frac{K_2}{K_1}\right]^2\\&=A_0\frac{T_c^0}{RT_c^2}\left[\left[\frac{\partial\rho}{\partial P}\right]_{T,x}^r\right]^{-1}\left[\frac{a_3b_2-a_1b_3}{a_3-a_1x}\right]^2\ .\end{aligned} \tag{5.29}$$

Using (5.1), (5.7), (5.8), and (5.11) one may conclude

$$\tilde{X}_A\simeq A_0\frac{T_c^0}{T_c}\left[RT_c\left[\frac{\partial\rho}{\partial P}\right]_{T,x}^r\right]^{-1}\left[\rho_cR\frac{dT_c}{dP}\right]^2\ . \tag{5.30}$$

It is worthwhile to note that Eq. (5.30) resembles Eq. (4.23) with K_2 given by (4.20) for the corresponding quantity X_A for dilute solutions: $(\partial\rho/\partial P)^r_{T,x}$ serves as $(\partial x/\partial\mu)^r_{P,T}$ and dT_c/dP serves as $dT_c/d\mu$.

Essentially the same expressions for $\tilde{X}_A$ can be obtained from Eq. (3.31) by considering the condition at which

$$RT_c^0\left[\left[\frac{\partial\rho}{\partial P}\right]_{T,\mu}^r\right]^{-1}K_2^2\chi_2\simeq\left[K_1+\rho_c\left[\frac{\partial x}{\partial\rho}\right]_{T,\mu}^r\right]^2\ . \tag{5.31}$$

For $\tau\ll\tilde{\tau}_2$ both the isothermal compressibility at constant composition and the osmotic compressibility at constant density diverges weakly. For $\tau\gg\tilde{\tau}_1$ $(\partial\rho/\partial P)_{T,x}$

does not diverge and in the intermediate range $\tilde{\tau}_2<\tau<\tilde{\tau}_1$ $(\partial\rho/\partial P)_{T,x}$ exhibits crossover behavior. The osmotic compressibility at constant density diverges weakly for $\tau\ll\tilde{\tau}_2$ and it diverges strongly for $\tau\gg\tilde{\tau}_1$, while exhibiting crossover behavior in the range $\tilde{\tau}_2<\tau<\tilde{\tau}_1$. For $\tau\gg\tilde{\tau}_2$ both $C_{P,x}$ and $C_{V,x}$ diverge weakly; for $\tau\ll\tilde{\tau}_2$ $C_{P,x}$ remains weakly divergent, while $C_{V,x}$ tends to a finite value.

VI. SPECIAL CRITICAL POINTS IN A PHASE DIAGRAM

On the critical locus of binary mixtures one may encounter peculiar points that are of special interest. Examples are points on the critical locus where $dT_c/dx=0$, $dP_c/dT=0$, or $dT_c/dP=0$ or where the critical line meets an azeotrope. In this section we shall show how the specific thermodynamic critical behavior near such points can be deduced from the generalized isomorphism developed in Sec. III.

A. Critical azeotropy

An azeotropic liquid mixture evaporates like a one-component fluid, since the coexisting vapor and liquid phases have identical composition. A phase diagram of a mixture with a critical azeotrope is shown in Fig. 5. At the azeotropic critical point [26]

$$\frac{dP_c}{dT}=\left[\frac{\partial P}{\partial T}\right]^c_{cxc}=\left[\frac{\partial P}{\partial T}\right]^c_{\rho=\rho_c,h_1=0} . \tag{6.1}$$

From Eqs. (4.14) and (6.1) we note that

$$\begin{aligned}K_1&\propto\left[\frac{\partial P}{\partial x}\right]^c_{T=T_c,h_1=0}\\&=\frac{dP_c}{dx}-\left[\frac{\partial P}{\partial T}\right]^c_{\mu=\mu_c,h_1=0}\frac{dT_c}{dx}=0 .\end{aligned} \tag{6.2}$$

It thus follows from (3.24) that at the azeotropic critical point

$$a_3=a_1x , \tag{6.3}$$

so that the strong scaling field h_1, given by (3.2), becomes

$$h_1=a_1(\Delta\mu_1+x\Delta\mu)+a_2\Delta T . \tag{6.4}$$

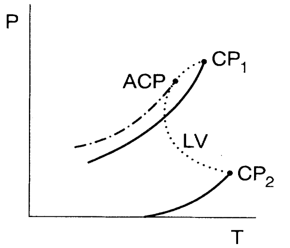

FIG. 5. Schematic phase diagram of a system with an azeotrope critical point (ACP). The solid curves indicate the vapor-pressure curves of the two pure components. The dotted curve indicates the liquid-vapor (LV) critical line connecting with the critical points CP_1 and CP_2 of the pure components. The dash-dotted curve indicates a line of azeotropic conditions meeting the critical line at the ACP with a common tangent.

Noting that $\mu_1=g-\mu x$, where g is the molar Gibbs free energy of the mixture, we have $\Delta\mu_1=\Delta g-x\Delta\mu-\mu\Delta x$, while $\Delta g=-S\Delta T+V\Delta P+\mu\Delta x$, where S and V are the molar entropy and the molar volume, respectively. As a consequence,

$$h_1=a_1\Delta g_0+a_2\Delta T \tag{6.5}$$

with

$$\Delta g_0=-S\Delta T+V\Delta P . \tag{6.6}$$

The term Δg_0 represents the Gibbs-free-energy difference of a quasi-one-component fluid with fixed composition. On comparing (6.5) with (2.13) we conclude that the scaling field h_1 has the same form as that of a one-component fluid. As a consequence, the isothermal compressibility diverges as the strong susceptibility χ_1, as it also does in a one-component fluid. This can be seen if one substitutes $K_1=0$ into Eq. (3.23) and neglects less singular terms. It can also be seen from the expression (4.17) for X_Γ, where $K_1=0$ implies $X_\Gamma=0$. The osmotic compressibility $(\partial x/\partial\mu)_{P,T}$ now diverges weakly as can be seen by substituting $a_3-a_1x=0$ into Eq. (3.19). The isobaric molar heat capacity $C_{P,x}\propto(\partial\rho/\partial P)_{T,x}$ which diverges as χ_1.

On the other hand the weak scaling field h_2 still retains a mixturelike form as given by Eq. (3.3). Hence, the isochoric specific heat capacity $C_{V,x}$ will again ultimately reach a finite value at the critical point as it does generally in mixtures.

B. Maximum or minimum critical temperature

Another special case is encountered when the locus of critical temperatures as a function of the concentration goes through a maximum or minimum. An example of a mixture for which the critical temperature $T_c(x)$ goes through a minimum is the system carbon dioxide+ethane [46]. At this minimum $dT_c/dx=0$, but $dP_c/dx\neq0$. Hence, the quantities K_1 and X_Γ now remain finite in accordance with (4.14) and (4.16). The condition $dT_c/dx=0$ implies $dT_c/d\mu=0$, so that from (4.5) and (4.6) $a_3=-a_1d\mu_{1c}/d\mu$ and $b_3=-b_1dT_c/d\mu$. Substitution of these results into Eq. (3.25) shows that in this case

$$K_2=0 . \tag{6.7}$$

Hence, it follows from (3.23) and (3.31) that $(\partial\rho/\partial P)_{T,x}$ and $(\partial x/\partial\mu)_{\rho,T}$ now remain finite at the critical point. Because $(\partial x/\partial\mu)_{\rho,T}$ remains finite, it can no longer compensate for the weakly divergent behavior of $(\partial s/\partial T)_{\rho,\mu}$ in Eq. (3.21), so that $C_{V,x}$ diverges asymptotically as χ_2. Because

$$C_{P,x}-C_{V,x}=\frac{T}{\rho^2}\left[\frac{\partial P}{\partial T}\right]^2_{\rho,x}\left[\frac{\partial\rho}{\partial P}\right]_{T,x} \tag{6.8}$$

and $(\partial\rho/\partial P)_{T,x}$ remains finite, $C_{P,x}$ diverges weakly just as $C_{V,x}$. The same observations have been made by Griffiths and Wheeler [6] and by Saam [7]. It is also implied by the crossover model developed by Jin, Tang, and Sengers for mixtures of carbon dioxide and ethane [21].

C. Reentrant critical point

A different special point is encountered when $dP_c/dT=0$. Such a point on the critical line, as indicated in Figs. 2 and 3, may be called a reentrant critical point (RCP) according to a nomenclature adopted in liquid-crystal phase transitions [47]. Below the reentrant critical pressure the one-phase (disordered phase) returns upon lowering the temperature at constant pressure. At such a reentrant critical point nothing special happens with the isochoric molar heat capacity $C_{V,x}$, which has a finite limiting value, nor with the isothermal compressibility which asymptotically diverges weakly as in the general case. Since at the reentrant critical point $(\partial P/\partial T)^c_{V,x}=dP_c/dT=0$, the isobaric molar heat capacity $C_{P,x}$ remains finite.

Near points of extremum pressure or extremum temperature one observes a doubling of the critical-exponent values along certain thermodynamic paths depending on the character of the extremum [48–56]. To elucidate the origin of this exponent doubling we treat the temperature T as the hidden field in the vicinity of the point where $dP_c/dT=0$, so that

$$h_1=a_1(T)\Delta\mu_1(T)+a_3(T)\Delta\mu(T)$$

$$\simeq a_1\Delta\mu_1+a_3\Delta\mu-\left[a_1\frac{d\mu_{1c}}{dT}+a_3\frac{d\mu_c}{dT}\right]\Delta T_c\ , \qquad (6.9)$$

$$h_2=b_2(T)\Delta\mu_1(T)+b_3(T)\Delta\mu(T)$$

$$\simeq b_2\Delta\mu_1+b_3\Delta\mu-\left[b_2\frac{d\mu_{1c}}{dT}+b_3\frac{d\mu_c}{dT}\right]\Delta T_c\ , \qquad (6.10)$$

where ΔT_c is the difference of two values of T_c on the critical line. In linear approximation

$$\Delta P=\rho_c\Delta\rho_1+\rho_c S_c\Delta T+\rho_{2c}\Delta\mu\ . \qquad (6.11)$$

On a path of constant pressure P, i.e., along an isobar, relation (6.11) becomes

$$\Delta\mu_1=-(S_c\Delta T+x_c\Delta\mu)\ . \qquad (6.12)$$

We can consider $\Delta\mu$ as a function of T, P, and x. Again in linear approximation

$$\Delta\mu=\left[\frac{\partial\mu}{\partial T}\right]_{P,x}\Delta T+\left[\frac{\partial\mu}{\partial P}\right]_{T,x}\Delta P+\left[\frac{\partial\mu}{\partial x}\right]_{P,T}\Delta x\ . \qquad (6.13)$$

Since $(\partial\mu/\partial x)_{P,T}=0$ at the critical point, we have along the critical isobar

$$\Delta\mu=\left[\frac{\partial\mu}{\partial T}\right]_{P,x}\Delta T\ . \qquad (6.14)$$

If the critical isobar corresponds to the point where $dP_c/dT=0$, then $\Delta T=\Delta T_c$ in first approximation. Substitution of (6.12) and (6.14) into the expressions (6.9) and (6.10) for the scaling fields yields

$$h_1=-a_1\left[S_c+x_c\frac{d\mu_c}{dT}+\frac{d\mu_{1c}}{dT}\right]\Delta T_c\ , \qquad (6.15)$$

$$h_2=-b_2\left[S_c+x_c\frac{d\mu_c}{dT}+\frac{d\mu_{1c}}{dT}\right]\Delta T_c\ . \qquad (6.16)$$

On the other hand it follows from Eq. (3.1) that the condition $dP_c/dT=0$ implies

$$S_c+x_c\frac{d\mu_c}{dT}+\frac{d\mu_{1c}}{dT}=0\ . \qquad (6.17)$$

Upon substitution of (6.17) into (6.15) and (6.16) we see that the linear terms in the expressions for the scaling fields vanish near the critical reentrant point and the leading asymptotic scaling-field behavior is determined by the quadratic terms arising from an expansion of the coefficients in Eq. (6.9) and (6.10) and leading to the phenomenon of exponent doubling. For example, the strong susceptibility χ_1 near the point $dP_c/dT=0$ will vary along the critical isobar as

$$\chi_1=h_2^{-\gamma}f''(z)\propto\tau^{-2\gamma}f''(z)\ . \qquad (6.18)$$

Similarly all other critical exponents in the power laws along the critical isobar are doubled.

D. Double critical point

A double critical point is a point where a line of lower critical points and a line of upper critical points merge. The definition of a double critical point is not unique [57]. It can manifest itself in the phase diagram either as a reentrant critical point where $dP_c/dT=0$ or as a critical point corresponding to a temperature minimum as in Fig. 4. The first case, also referred to as a hypercritical point [3,54] is characteristic for closed-loop consolute phase diagrams and a doubling of the critical exponents occurs along the path $P=$const [49–56]. The second case, also referred to as a double plait point dividing the vapor-liquid critical line and the gas-gas critical line, leads to a doubling of the critical exponents along the path $T=$const [48]. Therefore, the two cases reduce to those considered above.

VII. CROSSOVER FROM THE ONE-COMPONENT VAPOR-LIQUID CRITICAL LIMIT TO THE MIXTURE LIQUID-LIQUID CRITICAL LIMIT

We consider here the case that the critical locus is a continuous line which starts at the vapor-liquid critical point of the solvent and which terminates in a consolute critical endpoint as indicated in Fig. 3. The physical fields in expressions (3.2) and (3.3) exchange their roles: $\Delta\mu$ plays the role of hidden field in dilute solutions, but of the ordering field in "incompressible" liquid mixtures, while $\Delta\mu_1$ does the same in the opposite cases. The variation of the coefficients a_1 and a_3 along the critical locus results in the transformation of the order parameter ϕ_1 from density to concentration, while the variation of the coefficients b_2 and b_3 is responsible for the transformation of the origin of the nonasymptotic corrections [cf. Eqs. (2.22) and (5.14)]. Such an exchange occurs in both scaling fields h_1 and h_2 which are controlled by the variation of the coefficients a_1 and a_3 and of b_2 and b_3 along the critical line.

The coefficient a_1 in units of $(RT_c)^{-1}$ will vary continuously from unity in accordance with Eq. (2.15) to zero in the incompressible liquid-mixture limit. On the other hand, the coefficient a_3 will vary from zero to one in the same units. To make this variation explicit, it is convenient to express the coefficients a_1 and a_3 in terms of polar coordinates [31,58],

$$a_1 = r(x)\cos\phi \ , \tag{7.1}$$

$$a_3 = r(x)\sin\phi \ , \tag{7.2}$$

where the angle ϕ varies from $\phi=0$ in the pure solvent limit $(x \to 0)$ and from $\phi=\pi/4$ in the pure solute limit $(x \to 1)$ to $\phi=\pi/2$ in the incompressible liquid-mixture limit. Hence

$$\frac{a_3}{a_1} = x - K_1 = \tan\phi \ . \tag{7.3}$$

Based on this approach we may suggest simple interpolation formulas for the coefficients a_1 and a_3 that are explicit functions of the concentration x and which incorporate the two limits on the critical line:

$$a_1 = r(x)\frac{1}{\sqrt{1+(x-K_1)^2}} \ , \tag{7.4}$$

$$a_3 = r(x)\frac{x-K_1}{\sqrt{1+(x-K_1)^2}} \ , \tag{7.5}$$

with a radius

$$r(x) = \frac{1}{RT_c(x)}\left[1+\frac{x(x-x_2)}{1-x_2}\right]^{1/2} \ , \tag{7.6}$$

where x_2 is the value of the concentration x in the incompressible liquid-mixture limit, which is assumed to correspond to CEP_2 in Fig. 3, while K_1 is given by Eq. (4.18). The difference $a_3 - a_1 x$ is then given by

$$a_3 - a_1 x = -a_1 K_1 = -r(x)\frac{K_1}{\sqrt{1+(x-K_1)^2}} \ . \tag{7.7}$$

In Fig. 6 we show the variation of the a_1 and $a_3 - a_1 x$ according to Eqs. (7.4) and (7.7), if we assume for simplicity that the behavior of K_1 along the critical line can be represented by

$$K_1 = -\frac{x(1-x)}{|x-x_2|} \ . \tag{7.8}$$

The limits $x=0$ and $x=1$ correspond to the critical points of the pure components, indicated by CP_1 and CP_2 in Fig. 3; $x=x_1$ and $x=x_2$, for which we have arbitrarily adopted the values $x_1=0.2$ and $x_2=0.5$ correspond to CEP_1 and CEP_2 in Fig. 3. The interval $x_1 < x < x_2$ corresponds to a miscibility gap where the critical line does not exist.

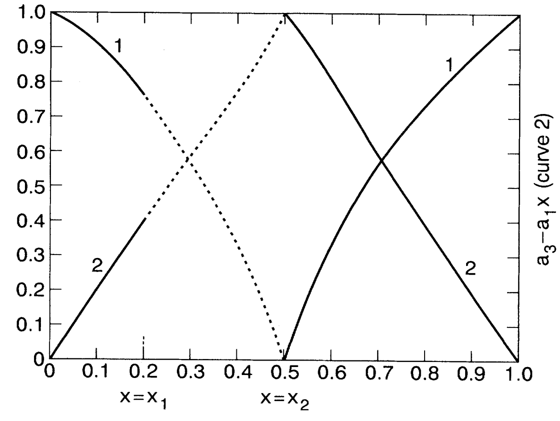

FIG. 6. Variation of the coefficient a_1 (curve 1) and of $a_3 - a_1 x$ (curve 2) in units of RT_c along the critical line as a function of the concentration according to Eqs. (7.4) and (7.7) with a simple approximation (7.8) for K_1. The limits $x=0$ and $x=1$ correspond to the critical points of the pure components (CP_1 and CP_2 in Fig. 3); $x=x_1=0.2$ corresponds to CEP_1 in Fig. 3 and $x=x_2=0.5$ corresponds to CEP_2 in Fig. 3. The dashed curves between x_1 and x_2 correspond to a miscibility gap, where the critical line does not exist.

The behavior of K_1 as given by Eq. (7.8) assumes that there are no special points on the critical line except the one-component limits and the incompressible liquid-mixture limit. The possible existence of special points, such as an azeotropic critical point or points of extremum of $T_c(x)$ and $P_c(x)$ as a function of x will change the behavior of $K_1(x)$ s a function of x and, hence, will lead to a corresponding change of the crossover behavior of the coefficients a_1 and a_3 through Eqs. (7.4) and (7.5).

VIII. DISCUSSION

Most accurate experiments on near-critical binary liquid mixtures have been performed in the immediate vicinity of consolute end points, where the experimental variables $T-T_c$ and $x-x_c$ at constant pressure are very close to the isomorphic variables h_2 and ϕ_1. One then finds indeed the asymptotic universal critical behavior of such properties as the osmotic compressibility [59–66], the isobaric specific heat [67,68], and the coexistence curve [69–72]. Asymmetric corrections due to a difference between $T-T_c$ and h_2 and between $x-x_c$ and ϕ_1 are difficult to detect experimentally in the commonly used temperature range $(T-T_c)/T_c$ varying from 10^{-5} to 10^{-2}.

There are some investigations of the isochoric specific heat capacity $C_{V,x}$ in liquid mixtures near the consolute point under nonisomorphic experimental conditions, i.e., at constant x and ρ [3,73,74]. The results of these studies confirm the conclusion of Sec. V that for liquid mixtures with a weak dependence of the critical temperature T_c on the pressure the temperature range τ_2 where a renormalization of the critical exponent for $C_{V,x}$ occurs is very small. In the case of a mixture of liquid methanol and cyclohexane, for which the essential parameter entering in (5.30) $\rho R(dT_c/dP) \simeq 0.03$, one observes a weak but noticeable depression of the critical behavior of $C_{V,x}$ as compared to the singular behavior of $C_{P,x}$ [74]. In the case of a mixture of liquid iso-octane and nitroethane, for which $\rho R(dT_c/dP)$ is lower by an order of magnitude, both $C_{P,x}$ and $C_{V,x}$ exhibit identical singular behavior [3,73].

In contrast to liquid mixtures near consolute points, the asymptotic thermodynamic behavior of fluid mixtures near vapor-liquid critical loci have not been investigated so extensively with the exception of such simple mixtures as $^3\text{He}+^4\text{He}$ [15] and $CO_2+C_2H_6$ [22,75,76]. For fluid mixtures in which the critical points of the one-component limits are smoothly connected by a vapor-liquid critical line, i.e., mixtures exhibiting type-I phase behavior, one commonly applies the isomorphism principle in the simplified form where the scaling fields h_1 and h_2 are related to two physical fields $\Delta\mu$ and ΔT only, while μ, or equivalently $\zeta = e^{\mu/RT}/(1+e^{\mu/RT})$, is treated as the hidden field [9,10,22]. The critical parameters and the coefficients a_1, a_2 and b_1, b_2 in Eqs. (3.2) and (3.3) depend parametrically on the hidden field ζ, while a_3 and b_3 are taken to zero. However, even in the case of fluid mixtures with type-I phase behavior we expect that the introduction of the more general expressions (3.2) and (3.3) for the scaling fields with $a_3 \neq 0$ and $b_3 \neq 0$ will become necessary when the difference between the critical temperatures of the two pure fluid components becomes large.

Some studies of the critical behavior of dilute solutions have been reported. For instance, in dilute solutions of n-heptane in ethane, in which the concentration dependence of T_c is very steep, the renormalization of the critical exponent of the isochoric specific heat capacity has been observed [76]; for a solution with a n-heptane mole fraction $x=0.03$, the crossover temperature τ_2 defined by (4.21) is between 10^{-2} and 10^{-3}, and the apparent critical exponent α is indeed renormalized at $\tau < \tau_2$.

Studies of the isochoric specific heat capacity of mixtures of $CO_2+C_2H_6$ near the azeotropic critical point [76] and of the osmotic compressibility of fluid mixtures near double critical points of two kinds, namely, near a double plait point which corresponds to a temperature minimum on the critical line [48] and near a liquid-liquid hypercritical point [56] also show agreement with the behavior implied by our general isomorphism approach. In particular the doubling of the exponent γ and the crossover from the universal value of γ to its doubled value has been observed for a mixture of polystyrene and acetone [56] and for a pseudobinary mixture of guaiacol and glycerol-water [77].

Unfortunately, experimental studies of the actual crossover of the thermodynamic properties of fluid mixtures along the critical line from vapor-liquid behavior to liquid-liquid behavior are not yet available. The present paper yields some quantitative predictions of such a crossover behavior which can be tested experimentally. Promising systems for such a study would be mixtures of hydrocarbons with widely different molecular masses such as, e.g., methane and n-hexane.

IX. CONCLUSION

We have formulated a general procedure for implementing the principle of critical-point universality to specify the critical thermodynamic behavior of fluid mixtures. The approach goes beyond the original work of Griffiths and Wheeler [6], of Saam [7], and of Anisimov, Voronel, and Gorodetskii [8] in that it incorporates the continuous crossover transition of relevant scaling fields to hidden fields and vice versa. We recover the known critical thermodynamic behavior in the vicinity of critical points where special conditions are satisfied.

In addition, we have proposed general crossover expressions (7.4) and (7.5) for the coefficients that are responsible for the transformation of the strong scaling field and of the order parameter as one moves along the critical line. These expressions contain only one system-dependent parameter K_1 as defined by Eq. (4.18) and they include all general and special critical behavior, such as the one-component limits, the "incompressible" consolute limit, the azeotropic critical point, and the points of extremum of T_c and P_c as a function of x, depending on the actual value of K_1. The approach can also be used to elucidate the critical behavior of transport properties of fluid mixtures and can be generalized to deal with critical behavior of multicomponent mixtures as well.

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