

Joint description of the vapor–liquid and consolute critical phenomena

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A generalized formulation of the principle of critical-point universality for binary mixtures is proposed. Just as for one-component fluids, the critical behavior of binary mixtures is determined by two scaling fields: a strong ordering field conjugate to the order parameter and a weak field. Both scaling fields are linear combinations of three field variables which are related to the temperature and the chemical potentials of the two components with coefficients that vary along the critical line. © 1994 American Institute of Physics.

Binary mixtures exhibit numerous phase diagrams.¹ One of them, shown in Fig. 1, is of a special interest, because in this case the line of vapor–liquid critical points, starting at the critical point CP_1 of the solvent, transforms smoothly into a line of consolute points (liquid–liquid critical points) which terminate at the critical end point CEP_1 . At CEP_1 the two critical liquid phases and a noncritical vapor phase coexist. How can the gradual transformation of the near-critical physical properties of a highly compressible system near the vapor–liquid critical point to those of an almost incompressible system near the consolute point be described? The approach presented here is based on the principle of critical-point universality and provides a joint description of these two types of critical phenomena.

The principle of critical-point universality implies that the thermodynamic behavior of near-critical one-component fluids and of “incompressible” binary mixtures near the consolute (liquid–liquid) critical point is characterized by two relevant scaling fields, a strong ordering field associated with the order-parameter fluctuations, and a weak temperature-like field associated with energy fluctuations. We denote these fields as h_1 and h_2 . According to Pokrovskii,² we have

$$h_1 = (g - g_c) + a(T - T_c), \quad (1)$$

$$h_2 = (T - T_c) + b(g - g_c). \quad (2)$$

Here g is the chemical potential (molar Gibbs free energy) for one-component fluids or $g = \mu = \mu_2 - \mu_1$, the difference between the chemical potentials of the two components, for “incompressible” binary mixtures. T is the temperature, a and b are system-dependent coefficients, and the subscript c indicates values at the critical point. Mixing of

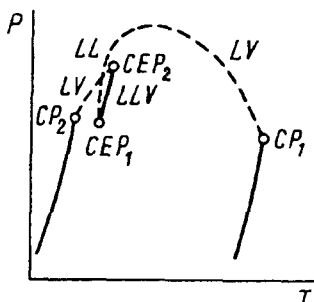


FIG. 1. Phase diagram of a methane-hexane mixture. CP_1 is the critical point of hexane and CP_2 the critical point of methane; CEP_1 is the critical end point on the liquid-liquid critical line, and CEP_2 the critical end point on the vapor-liquid critical line; LV represents the liquid-vapor critical line; LL denotes the critical locus of the consolute points (liquid-liquid equilibrium); LLV indicates the line of the three-phase equilibrium (two liquid phases and a vapor phase coexist) which terminates at the critical end points.

field variables to account for asymmetry between the two phases does not affect the asymptotic critical behavior of one-component fluids and of “incompressible” liquid mixtures. Such mixing leads to corrections to the asymptotic behavior (for example, a “singular diameter” of the coexisting curve).³

In this paper we show that in binary solutions the mixing of field variables leads to more significant circumstances which change the asymptotic critical behavior in some cases. According to the isomorphism hypothesis,^{4,5} a small impurity (dilute solutions near the vapor-liquid critical point) and a small compressibility of liquid mixtures near consolute points can be incorporated in the definitions of h_1 and h_2 by introducing “hidden fields” which are conjugate to the “hidden densities,” specifically, the concentration of a solute in the former case and the total density in the latter case. The field conjugate to the concentration is μ and the field conjugate to the density is μ_1 (chemical potential of the solvent).^{5,6} Thus the critical parameters in (1) and (2) appear to be functions of μ for the vapor-liquid critical point of a dilute solution and of μ_1 for the consolute point of weakly compressible liquids. How can liquid-vapor critical phenomena and liquid-liquid critical phenomena be incorporated into a general unified picture?

To extend the principle of critical-point universality to the general case we assume that the thermodynamic behavior of mixtures is still characterized by two scaling fields h_1 and h_2 . However, following Saam,⁷ the scaling fields are now linear combinations of three physical variables $\Delta T = T - T_c$, $\Delta\mu_1 = \mu - \mu_{1c}$, and $\Delta\mu = \mu - \mu_c$:

$$h_1 = a_1 \Delta\mu_1 + a_2 \Delta T + a_3 \Delta\mu, \quad (3)$$

$$h_2 = b_1 \Delta T + b_2 \Delta\mu_1 + b_3 \Delta\mu. \quad (4)$$

It should be noted that all system-dependent parameters in these expressions, 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 position on the critical line. We emphasize again that the coefficients a_i and b_i are now system-dependent functions of the position on the critical line and may vanish at certain points.

In binary mixtures the density of the relevant thermodynamic potential, the pressure $P = -\Omega/V$, is a function of three variables, namely, the temperature T , the chemical potential μ_1 , and the chemical potential difference $\mu = \mu_2 - \mu_1$:

$$dP = \rho S dT + \rho d\mu_1 + \rho_2 d\mu, \quad (5)$$

where $\rho_2 = \rho x$ is the partial density of the solute, ρ is the total molar density, and S is the molar entropy. As usual, P can be separated into a singular part and a regular part:⁶

$$P = P_s(h_1, h_2) + P_r(T, \mu_1, \mu), \quad (6)$$

where the regular part is an analytic function of the three field variables T , μ_1 , and μ . The dimensionless singular part of the pressure, $\tilde{P}_s = P_s / \rho_c^{(0)} R T_c^{(0)}$, has the same universal form as for a one-component fluid ($\rho_c^{(0)}$ and $T_c^{(0)}$ are the critical density and the critical temperature of the pure solvent, and R is the molar gas constant) and it satisfies asymptotically a scaling equation of the form⁸

$$\tilde{P}_s(h_1, h_2) = h_2^{2-\alpha} f(h_1/h_2^{\beta+\gamma}), \quad (7)$$

where α , β , and γ are the critical exponents.

The three physical densities $\Delta\rho = \rho - \rho_c$, $\Delta\rho_2 = \rho_2 - \rho_{2c}$, and $\Delta s = s - s_c$ can be expressed as linear combinations of two densities φ_1 and φ_2 which are conjugate to h_1 and h_2 :

$$\Delta\rho = \rho_c^{(0)} R T_c^{(0)} (a_1 \varphi_1 + b_2 \varphi_2), \quad (8)$$

$$\Delta\rho_2 = \rho_c^{(0)} R T_c^{(0)} (a_3 \varphi_1 + b_3 \varphi_2), \quad (9)$$

$$\Delta s = \rho_c^{(0)} R T_c^{(0)} (a_2 \varphi_1 + b_1 \varphi_2). \quad (10)$$

On the path $h_1 = 0$, these densities behave as $\varphi_1 \propto h_2^\beta$ and $\varphi_2 \propto h_2^{1-\alpha}$. We can now define the universal susceptibilities; specifically, the "strong" susceptibility χ_1 and the "weak" susceptibility χ_2 :

$$\chi_1 = \left(\frac{\partial \varphi_1}{\partial h_1} \right)_{h_2} = h_2^{-\gamma} f''(z), \quad \chi_2 = \left(\frac{\partial \varphi_2}{\partial h_2} \right)_{h_1} = h_2^{-\alpha} \Psi(z), \quad (11)$$

where

$$\Psi(z) = (1 - \alpha)\psi(z) - (\beta + \gamma)z\psi'(z), \quad \psi(z) = (2 - \alpha)f(z) - (\beta + \gamma)zf'(z).$$

Strictly speaking, there is an additional universal susceptibility, namely, the cross susceptibility $\chi_{12} = \chi_{12} = (\partial \varphi_1 / \partial h_2)_{h_1} = (\partial \varphi_2 / \partial h_1)_{h_2}$. However, in zero field $h_1 = 0$ and in $h_2 > 0$ (one-phase region) χ_{12} vanishes.

In practice, these universal susceptibilities cannot be measured, but measurable thermodynamic properties can easily be expressed in terms of χ_1 and χ_2 by using the standard thermodynamic transformations. For example, the expressions for the isothermal compressibility and for the osmotic compressibility in the one-phase region above the critical point, $\chi_{12} = 0$, have the forms

$$\left(\frac{\partial x}{\partial \mu} \right)_{P,T} = R T_c^{(0)} [(a_3 - a_1 x)^2 \chi_1 + (b_3 - b_2 x)^2 \chi_2] + \left(\frac{\partial x}{\partial \mu} \right)_{P,T}^r, \quad (12)$$

$$\left(\frac{\partial \rho}{\partial P} \right)_{T,x} = \frac{L_{12} \chi_1 \chi_2 + L_1 \chi_1 + L_2 \chi_2}{1 + L_0 [(a_3 - a_1 x)^2 \chi_1 + (b_3 - b_2 x)^2 \chi_2]} + \left(\frac{\partial \rho}{\partial P} \right)_{T,x}^r, \quad (13)$$

where

$$L_0 = RT_c^{(0)} \frac{\rho_c^{(0)}}{\rho_c} \left[\left(\frac{\partial x}{\partial \mu} \right)_{P,T}^r \right]^{-1}, \quad L_{12} = RT_c^{(0)} L_0 (b_2 a_3 - a_1 b_3)^2,$$

$$L_1 = RT_c^{(0)} \left[a_1 - \frac{1}{\rho_c} \left(\frac{\partial \rho}{\partial x} \right)_{P,T}^r (a_3 - a_1 x) \right]^2,$$

$$L_2 = RT_c^{(0)} \left[b_2 - \frac{1}{\rho_c} \left(\frac{\partial \rho}{\partial x} \right)_{P,T}^r (b_3 - b_2 x) \right]^2.$$

Here $(\partial x / \partial \mu)_{P,T}^r$ and $(\partial \rho / \partial x)_{P,T}^r$ are the regular parts of $(\partial x / \partial \mu)_{P,T}$ and $(\partial \rho / \partial x)_{P,T}$, respectively. The main feature of the proposed approach is that the coefficients in Eqs. (3) and (4) vanish at certain specific points along the critical line. Writing the fields h_1 and h_2 in the form

$$h_1 = a_1 [\mu_1 - \mu_{1c}(\mu)] + a_2 [T - T_c(\mu)], \quad h_2 = b_1 [T - T_c(\mu)] + b_2 [\mu_1 - \mu_{1c}(\mu)], \quad (14)$$

we obtain the following expressions for the coefficients a_3 and b_3 :

$$a_3 = - \left(a_1 \frac{d\mu_{1c}}{d\mu} + a_2 \frac{dT_c}{d\mu} \right), \quad b_3 = - \left(b_2 \frac{d\mu_{1c}}{d\mu} + b_1 \frac{dT_c}{d\mu} \right). \quad (15)$$

Using the thermodynamic relation (5) and Eqs. (15), we can write the combinations $(a_3 - a_1 x)$ and $(b_3 - b_2 x)$ as follows:

$$a_3 - a_1 x = -a_1 \frac{dx}{d\mu_c} K, \quad b_3 - b_2 x = -b_2 \frac{dx}{d\mu_c} K + \left(b_2 \frac{a_2}{a_1} - b_1 \right) \frac{dT_c}{d\mu}, \quad (16)$$

where

$$K = \frac{1}{\rho_c RT_c} \left[\frac{dP_c}{dx} - \left(\frac{\partial P}{\partial T} \right)_{h_1=0}^c \frac{dT_c}{dx} \right] \quad (17)$$

and

$$\frac{1}{\rho_c} \left(\frac{\partial P}{\partial T} \right)_{h_1=0}^c = S_c - \frac{a_2}{a_1}. \quad (18)$$

Here $(\partial P / \partial T)_{h_1=0}^c$ is the critical value of this derivative taken along the coexistence curve, and S_c is the critical value of the molar entropy. Thus, the coefficient ratios a_3/a_1 and (b_3/b_2) take the form

$$\frac{a_3}{a_1} = x - RT_c \frac{dx}{d\mu_c} K, \quad (19)$$

$$\frac{b_3}{b_2} = x - RT_c \frac{dx}{d\mu_c} K + \frac{dT_c}{d\mu} \left(\frac{a_2}{a_1} - \frac{b_1}{b_2} \right). \quad (20)$$

Assuming that $(d\mu_c/dx) = RT_c(x)/x(1-x)$ on the critical line, we obtain

$$\frac{a_3}{a_1} = x - x(1-x)K, \quad (21)$$

$$\frac{b_3}{b_2} = x - x(1-x) \left[K - \frac{1}{RT_c} \frac{dT_c}{dx} \left(\frac{a_2}{a_1} - \frac{b_1}{b_2} \right) \right]. \quad (22)$$

Equations (21) and (22) describe the variation of these coefficients along the critical line, including the singular points.

a) For the one-component limits ($x=0$ and $x=1$) we have

$$RT_c a_1 \rightarrow 1 \quad \text{and} \quad a_3 \propto b_3 \propto x \rightarrow \begin{cases} 0 \\ 1 \end{cases}.$$

Therefore, at $h_1=0$ and $h_2^y \gg x(1-x)$ far away from the critical point we have

$$\left(\frac{\partial x}{\partial \mu} \right)_{P,T} \propto \left(\frac{\partial x}{\partial \mu} \right)_{P,T}^r \propto x(1-x), \quad \left(\frac{\partial \rho}{\partial P} \right)_{T,x} \propto \chi_1 \propto h_2^{-\gamma}. \quad (23)$$

Close to the critical point [$h_2^\alpha \ll x(1-x)$] we have

$$\left(\frac{\partial x}{\partial \mu} \right)_{P,T} \propto \chi_1 \propto h_2^{-\gamma}, \quad \left(\frac{\partial \rho}{\partial P} \right)_{T,x} \propto \chi_2 \propto h_2^{-\alpha}. \quad (24)$$

b) The critical azeotropic mixture ($K=0$) is

$$\left(\frac{\partial \rho}{\partial P} \right)_{T,x} \propto \chi_1 \propto h_2^{-\gamma}, \quad \left(\frac{\partial x}{\partial \mu} \right)_{P,T} \propto \begin{cases} \chi_2 \propto h_2^{-\alpha}, & h_2^\alpha \ll x(1-x) \\ \left(\frac{\partial x}{\partial \mu} \right)_{P,T}^r, & h_2^\alpha \gg x(1-x) \end{cases}. \quad (25)$$

(c) The extremum in the critical temperature ($dT_c/dx=0$) is

$$\frac{a_3}{a_1} = \frac{b_3}{b_2} = x - x(1-x) \frac{1}{\rho_c RT_c} \frac{dP_c}{dx},$$

$$L_{12} = 0, \quad L_2/L_1 = (b_2/a_1)^2,$$

and the isothermal compressibility behaves as

$$\left(\frac{\partial \rho}{\partial P} \right)_{T,x} \propto \begin{cases} \chi_1 \propto h_2^{-\gamma}, & h_2^y \gg x(1-x) \\ \text{const}, & h_2^y \ll x(1-x). \end{cases} \quad (26)$$

d) The consolute point in the “incompressible” limit

$$RT_c a_3 \rightarrow 1 \quad \text{and} \quad a_1, b_2 \propto \frac{1}{K} \propto \frac{dx}{dP} \rightarrow 0,$$

$$L_{12} \rightarrow 0, \quad L_2/L_1 = (b_3/a_3)^2,$$

$$\left(\frac{\partial x}{\partial \mu} \right)_{P,T} \propto \chi_1 \propto h_2^{-\gamma}, \quad \left(\frac{\partial \rho}{\partial P} \right)_{T,x} \propto \left(\frac{\partial \rho}{\partial P} \right)_{T,x}^r \rightarrow 0. \quad (27)$$

We conclude that the proposed generalization of the scaling fields in the form of Eqs. (3) and (4) describes crossover behavior of the thermodynamic properties of near-critical binary mixtures when the critical line gradually transforms from the vapor–liquid critical locus in highly compressible fluids to the liquid–liquid critical line in almost incompressible liquid mixtures. Because of the crossover behavior of the relevant coefficients, given by Eqs. (21) and (22), the physical fields in expressions (3) and (4) change their roles: $\Delta\mu$ plays the role of the hidden field in dilute solutions and it plays the role of the ordering field in “incompressible” liquid mixtures, while the $\Delta\mu_1$ field does the same in the opposite cases. The thermodynamic properties exhibit crossover behavior, depending on the position of the critical point in the critical locus. Further experimental tests of the predicted behavior would be very useful.

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