A JOINT DESCRIPTION OF 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 related to the temperature and the chemical potentials of the two components with coefficients that vary along the critical line.

Binary mixtures exibit numerous phase diagrams [1]. One of them, presented in figure, 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) terminating at a critical endpoint CEP_1. In CEP_1 two critical liquid phases and a noncritical vapor phase coexist. Thus the question arises how to describe 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. 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.
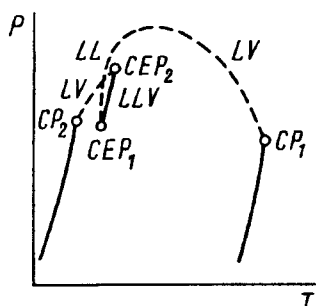

Fig.1.Phase diagram of a methane-hexane mixture. CP_1 is the critical point of hexane and CP_2 the critical point of methane; CEP_1 is the critical end point on a liquid-liquid critical line, and CEP_2 the critical end point on a vapor-liquid critical line; LV represents a liquid-vapor critical line; LL the critical locus of consolute points (liquid-liquid equilibrium); LLV indicates the line of three-phase equilibrium (two liquid phases and a vapor phase are in coexistence) terminating in critical end points

The principle of critical-point universality implies that the thermodynamic behavior of near-critical one-compoment 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]

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

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

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 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 only 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 changing in some cases the asymptotic critical behavior. 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" conjugate to "hidden densities", namely 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 conjugates 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. The question arises: 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 $\Delta \mu = \mu - \mu_c$:

$$h_1 = a_1 \Delta \mu_1 + a_2 \Delta T + a_3 \Delta \mu \quad , \tag{3}$$

$$h_2 = b_1 \Delta T + b_2 \Delta \mu_1 + b_3 \Delta \mu \quad . \tag{4}$$

One should note 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. Let us emphasize once more that all 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 ponetnials difference $\mu = \mu_2 - \mu_1$:

$$dP = \rho S dT + \rho d\mu_1 + \rho_2 d\mu, \tag{5}$$

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

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

where the regular part is an analytic function of the three field variables T, μ_1 and μ. The dimensionless singular part of 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 form [8]:

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

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 conjugate to h_1 and h_2:

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

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

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

On the path $h_1 = 0$ these densities behave as $\varphi_1 \propto h_2^{\beta}$ and $\varphi_2 \propto h_2^{1-\alpha}$. Now we may define universal susceptibilities, namely a "strong" susceptibility χ_1 and a "weak" susceptibility χ_2:

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

with

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

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

In practice, one cannot measure these universal susceptibilities, but one can easily express measurable thermodynamic properties in terms of χ_1 and χ_2 using usual thermodynamic transformations. As an 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 following forms:

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

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

where

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

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

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

and where $\left(\frac{\partial x}{\partial\mu}\right)_{P,T}^r$ and $\left(\frac{\partial\rho}{\partial x}\right)_{P,T}^r$ are the regular parts of $\left(\frac{\partial x}{\partial\mu}\right)_{P,T}$ and $\left(\frac{\partial\rho}{\partial x}\right)_{P,T}$,

respectively. The main feature of the proposed approach is that the coefficients in (3)-(4) vanish at certain specific points along the critical line. Presenting the fields h_1 and h_2 in the form

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

one can obtain for the coefficients a_3 and b_3

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

With the thermodynamic relation (5) and Eqs.(15) the combinations $(a_3 - a_1 x)$ and $(b_3 - b_2 x)$ can be written as

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

with

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

and

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

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

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

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

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

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

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

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

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

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

Therefore at $h_1 = 0$ and at $h_2^\gamma \gg x(1-x)$ far away from the critical point:

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

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Close to the critical point $(h_2^\alpha \ll x(1-x))$:

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

b) critical azeotropic mixture (K=0)

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

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

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

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

and the isothermal compressibility behaves as

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

d) consolute point in the "incompressible" limit

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

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

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

We conclude that the proposed generalization of the scaling fields in the form of Eqs.(3) and (4) provide the 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. Due to 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 of the ordering field in "incompressible" liquid mixtures while $\Delta\mu_1$ field does the same in the opposite cases. The thermodynamic properties exhibit crossover behavior depending on the position of the critical point on the critical locus. Further experimental tests of the predicted behavior would be very interesting.

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