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Universal Scaling Form of the Equation of State of a Critical Pure Fluid[1]

Y. Garrabos,[2, 3] B. Le Neindre,[4] R. Wunenburger,[2] C. Lecoutre-Chabot,[2] and D. Beysens[5, 6]

Close to the liquid gas critical point, the linear treatment of the symmetrical one-component Φ^4 model to observe the fluid-restricted universality of the subclass of pure fluids is reversed. The comparison with the fitting results obtained from the recent applications of the crossover description to CO_2, CH_4, C_2H_4, C_2H_6, R134a, SF_6, and H_2O confirms that the dimensionless characteristic two scale factors involved in this description are: (a) the critical compressibility factor and (b) the slope at the critical point of the reduced potential $\frac{P}{T}\frac{T_c}{P_c}$ along the critical isochore. For the two-phase domain along the critical isochore, a precise formulation for the extension range of the fluid-restricted universality is given in terms of the reduced scaling size $\ell^{*-}=\frac{\xi^-}{a_c}$ of the critical density fluctuations, expressed as a function of the dilated scaling field which measures the distance to the critical point below T_c. The explicit definition of the microscopic length scale $a_c=(\frac{k_BT_c}{P_c})^{\frac{1}{3}}$, which characterizes the short-range of the microscopic interaction, gives a correlative estimation of the crossover domain when $\xi^- \sim a_c$.

KEY WORDS: critical phenomena; equation of state; gas-liquid critical point; gas-liquid coexistence curve; scaling factors.

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[2] Equipe du Supercritique pour l'Environnement, les Matériaux et l'Espace, Institut de Chimie de la Matière Condensée de Bordeaux, Centre National de la Recherche Scientifique, UPR 9048, Université de Bordeaux I, 87 Avenue du Dr. Schweitzer, F-33608 Pessac Cedex, France.

[3] To whom correspondence should be adressed. E-mail: garrabos@icmcb.u-bordeaux.fr

[4] Laboratoire d'Ingéniérie des Matériaux et des Hautes Pressions, Centre National de la Recherche Scientifique, UPR 1311, Université Paris 13, Avenue Jean Baptiste Clément, F-93430 Villetaneuse, France.

[5] Equipe du Supercritique pour l'Environnement, les Matériaux et l'Espace, Service des Basses Températures, Commissariat à l'Energie Atomique, 17 Avenue des Martyrs, F-38054 Grenoble Cedex 9, France.

[6] Mailing address: ESEME-CEA, ICMCB, 87 Avenue du Dr. Schweitzer, F-33608 Pessac Cedex, France.

1. INTRODUCTION

Critical phenomena strike the imagination because they correspond to extreme values (infinity or zero) for some key properties of the system at its critical point [1]. The nature of these singular properties of critical systems is well understood in terms of the asymptotic critical phenomena universality [2]. A one-component fluid belongs to the $d = 3$, $n = 1$ universality class (d is the dimension of the space and n the dimension of the order parameter) for which the three-dimensional uniaxial Ising system near the Curie point is currently used as a *predictive model* [3]. Indeed, the singular asymptotic behavior of fluid properties satisfies scaling power laws with *universal* critical exponents and *universal* scaling functions near the liquid-gas critical point, revealing two independent amplitudes which are the only two system-dependent parameters [1–3]. As a matter of fact, the two-scale-factor universality is expected for all systems with short-ranged interaction having an isolated transition point [4]. But this universal behavior is valid only within the limit $\xi \Lambda_o \gg 1$, where the size ξ of critical fluctuations of the order parameter is greater than the molecular interaction range (here characterized by the microscopic length Λ_o^{-1}). With this limit is associated a domain, the asymptotic critical domain D_{AS}, within which some corrective contributions are assumed to be so small that they can be neglected [5]. Then, the size of D_{AS} where the asymptotic power laws apply can be nonuniversal [6].

More precisely, the analytical treatment by the renormalization group theory (RGT) relates the two renormalized relevant fields t (the temperature-like field) and h (the ordering field) of the symmetrical one-component Φ^4 model to the corresponding physical fields $\Delta\tau^*$ and Δh^* of the selected one-component Φ^4-like system as follows [6–9]:

$$t = \Theta\, \Delta\tau^* + O\{(\Delta\tau^*)^2, (\Delta\tau^*\, \Delta h^*)\} \tag{1a}$$

$$h = \Psi\, \Delta h^* + O\{(\Delta h^*)^2, (\Delta\tau^*\, \Delta h^*)\} \tag{1b}$$

Neglecting the second-order terms which account for analytic corrections to scaling, the linearized equations (1a) and (1b) involve the two-scale-factor universality through the introduction of the two nonuniversal constants Θ and Ψ. Θ characterizes the size of D_{AS} along the critical isocline for a constant zero value of the order parameter, while Ψ characterizes the size of D_{AS} along the critical isocline for a constant zero value of the ordering field conjugate to the order parameter. Each critical system is then characterized by two independent amplitudes of the asymptotic power laws, or, alternatively, by Θ and Ψ. In the absence of an explicit calculation of Θ and Ψ by the theory, the asymptotic power law behavior (even including the self-consistent Wegner's corrections to scaling [5]), is valid over an undetermined limit of D_{AS}. Then, the comparison between singular behavior of *equivalent* systems is not easy and it is difficult to know the nature of a possible criticality beyond D_{AS}. *A fortiori*, it is also difficult to develop a thermodynamic surface that not only incorporates the theoretical asymptotic critical behavior inside (or eventually outside) D_{AS}, but that also accounts for the correct regular behavior further away from the critical point. This challenge refers to the crossover problem whose complete theoretical description is very complex and is still the object of active research.

Within all the real critical points belonging to the $d = 3$, $n = 1$ universality class, only the liquid-gas critical point is an *isolated* point. This underlines once more the basic character of the liquid-gas critical transition of a pure fluid in the field of critical phenomena. Inverting the RGT method whose predictions are supposed valid for pure fluids, a selected one-component fluid (for example, xenon) can then be used as a *standard system* provided that the two relevant fields and the associated system-dependent factors Θ and Ψ are known independently. Applying the scale dilatations defined by Eqs. (1a, 1b) will give back the *fluid-restricted universality* of such a fluid subclass [10], [11]. This approach, originally proposed by one of us [11], [12] and briefly summarized below, is used in this paper in order: (a) to compare this fluid-restricted universality to the one implicitly given by the crossover description of critical fluids as proposed by Albright et al. [13, 14], and (b) to analyze the extension of D_{AS} in the coexisting two-phase domain.

2. PHENOMENOLOGICAL SCALE FACTORS FOR PURE FLUIDS

The basic idea of the phenomenological approach developed in Refs. 11 and 12 was to postulate that all the thermodynamics informations needed to describe the immediate vicinity of the liquid-gas critical point are contained in the location of this point and of its tangent plane to an appropriate characteristic surface. The addition of the critical isochoric thermal expansion coefficient at the critical point, γ_c, to the three classical critical parameters, temperature, T_c, pressure, P_c, and number density, $n_c (= \frac{\rho_c}{m_p})$, is then sufficient to complete this location. ρ_c is the critical mass density and m_p is the molecular mass of the constitutive particle. $\gamma_c = [\frac{dP_{\mathrm{sat}}}{dT}]_{\mathrm{CP}} = [(\frac{\partial P}{\partial T})_{\rho_c}]_{\mathrm{CP}}$, is the limiting slope at the critical point (CP), common to the saturated vapor-pressure curve (two-phase range) and to the critical isochore curve (one-phase range) in the $P-T$ diagram.

In order to obtain a closed description of the asymptotic singular behavior, these four input coordinates yield to four significant parameters, two of them $\beta_c = k_B T_c$ and $a_c = (\frac{k_B T_c}{P_c})^{1/3}$ being homogeneous to an energy and a length, respectively, and the other two Y_c and Z_c being nondimensional as shown below. k_B is the Boltzmann constant. The thermodynamic properties and static correlation functions of a known mass of a pure fluid are made dimensionless by expressing them in units of β_c and a_c. Then β_c and a_c define a fluid characteristic set of scaling units of energy and length, including only two intensive input coordinates, T_c and P_c. The basic modeling of a binary radial interaction by the short-ranged Lennard–Jones potential $\Phi_{\mathrm{LJ}}(r)$ yields their microscopic forms, $\beta_c \sim \varepsilon_{\mathrm{LJ}}$ and $a_c \sim 2 r_{e_{\mathrm{LJ}}}$, where $\varepsilon_{\mathrm{LJ}}$ is the depth of the potential energy at equilibrium position, $r_{e_{\mathrm{LJ}}}$. Except for quantum fluids, the characteristic length scale $a_c \sim \Lambda_o^{-1}$ is a measure of the range of the attractive dispersion forces [11]. The ratio $\frac{\xi}{a_c}$ provides a direct measurement between the size ξ of the critical fluctuations and the molecular interaction range a_c.

The two dimensionless characteristic factors Y_c and Z_c are defined from the other two remaining basic input coordinates, γ_c, and $n_c = \frac{\rho_c}{m_p}$. They are made nondimensional through the following equations [11]:

$$Y_c = \gamma_c \frac{T_c}{P_c} - 1 \tag{2}$$

$$Z_c = \frac{P_c}{n_c k_B T_c} = \frac{4\pi}{3} \frac{1}{n_{i_c}} \tag{3}$$

Note that Z_c is the usual critical compressibility factor. As emphasized by the second equality in Eq. (3), the inverse quantity $\frac{1}{Z_c}$ is proportional to the critical number of interacting particles, $n_{i_c} = n_c v_{i_0}$, summed in the scale unit of the spherical volume, $v_{i_0} = \frac{4}{3}\pi a_c^3$. v_{i_0} represents the critical interaction volume of radius a_c (the interaction range), formally equivalent to the critical cell unit of each spin in a spin system, or to the critical lattice volume of each site in the lattice gas system. We will return on the physical meaning of Y_c in Section 3.

The explicit forms of Eqs. (1a, 1b) now depend on the choices made for the reduced singular free energy density analogous to the singular free energy for the three-dimensional Ising model. An extensive literature addresses this problem, mainly to exhibit the non-symmetrical character of pure fluids, and to choose the product μn (where μ is the chemical potential per particle, conjugate to the number density $n = \frac{\rho}{m_p}$) as density of the symmetrical potential. We are only concerned here with the thermodynamic analogies [3], [6] that stipulate $\Delta\mu^* = \mu^* - \mu_c^* = [\frac{\mu}{k_B T_c} - \frac{\mu_c}{k_B T_c}]$ as an external ordering field, conjugate to the order parameter, $\Delta n^* = n^* - n_c^* = (\rho - \rho_c)\frac{k_B T_c}{m_p P_c}$ ($\Delta\mu^*$ is analogous to the reduced magnetic field H^* for the three-dimensional Ising model ($\Delta\mu^* \sim \Delta h^*$ in Eq. (1b)), while Δn^* is analogous to the reduced magnetization M^* of this model). Here, the reduced number density, $n^* = \frac{\rho}{\rho_c Z_c}$, differs from the usual dimensionless mass density, $\frac{\rho}{\rho_c}$. Then, for the one-component fluids, the usual physical field parameters are $\Delta\tau^* = \frac{T}{T_c} - 1$, and $\Delta n^* = \frac{1}{Z_c}\Delta\rho^*$ (with $\Delta\rho^* = \frac{\rho}{\rho_c} - 1$). They are dilated in their scaling form as defined by Eqs. (1a, 1b) in the RGT linear treatment, introducing the corresponding fluid scale factors Θ (along the critical isochore) and Ψ (along the critical isotherm) that read [12]:

$$\Theta = Y_c \tag{4a}$$

$$\Psi = (Z_c)^{-\frac{3}{2}} = (\Psi_\rho\, Z_c)^{-1} \qquad (\text{with } \Psi_\rho = (Z_c)^{\frac{1}{2}}) \tag{4b}$$

In the second form of Eq. (4b), the scale factor $\Psi_\rho = (\Psi Z_c)^{-1}$ dilates the usual reduced density difference $\Delta\rho^*$. The corresponding scale dilatations for the order parameter m, conjugate to h, are

$$m = \Psi^{-1}\,\Delta n^* = (Z_c)^{\frac{3}{2}}\,\Delta n^* = \Psi_\rho\,\Delta\rho^* = (Z_c)^{\frac{1}{2}}\left(\frac{\rho}{\rho_c} - 1\right) \tag{5}$$

It is now easy to show that two selected independent amplitudes of the standard pure fluid, hereafter denoted $\frac{\xi_o^+}{a_c}$ and D^c, and its corresponding two scale factors Y_c and Z_c, are unequivocally linked through the following two master combinations [11], [12]:

$$\left(\frac{\xi_o^+}{a_c}\right)^{\frac{1}{\nu}} Y_c = Y_G \tag{6a}$$

$$(D^c)^{\frac{-2}{3(\delta+1)}} Z_c = F_G \tag{6b}$$

$\frac{\xi_o^+}{a_c}$ is the amplitude (ν being the corresponding universal critical exponent) of the dimensionless correlation length divergence along the critical isochore in the one-phase region. D^c is the amplitude (δ being the corresponding universal critical exponent) of the asymptotic shape of the critical isotherm for $\Delta\mu^*$. Due to their scale-factor nature, the phenomenological constants Y_G and F_G obtained from this standard pure fluid will be the same for all pure fluids [11], leading to the definition of the restricted universality of the corresponding fluid subclass. Then, the complete set of the dimensionless asymptotic amplitudes of each pure fluid can be obtained from the complete set of the $d = 3$, $n = 1$ universal ratios predicted by the

RGT [8, 16]. In a similar way, a preliminary estimate [12] of the first-term amplitude for the dilated confluent correction to scaling allows to calculate all the others amplitudes from the corresponding theoretical universal ratios [8, 17]. In Refs. 16 and 17 we give only the numerical values of the amplitudes involved in the present work, which incorporate some minor adjustments [11], [12] due to the recent theoretical calculations of the universal ratios [8].

Note that the RGT [10] can also be used to calculate universal amplitudes appearing in the power law scaling functions. For example, the dimensionless correlation length ℓ^{*+} along the critical isochore above T_c has been obtained as an explicit Wegner expansion of the dimensionless scaling field t as follows:

$$\ell^{*+} = Z_{\xi}^{+}(t)^{-\nu}\,[1 + a_{\xi}^{+}(t)^{\Delta} + \cdots] \tag{7}$$

where the Wegner expansion of the corrections to scaling is limited here to the first-order. Δ is the universal critical exponent of the first confluent correction to scaling. In Eq. (7), Z_{ξ}^{+} and a_{ξ}^{+} can be estimated from the nonlinear analysis of the Φ^4 model. However, as previously analyzed in Ref. 10 and, as shown by the explicit a_c factor in the first master equation (6a), the comparison between experiments and field theory calculations allows a suitable choice of the characteristic length to be found for the reduction into dimensionless quantities. Using our suitable choice of a_c, we identify ℓ^{*+} with the ratio $\frac{\xi^{+}}{a_c}$ and obtain the following relation between the numerical constants Z_{ξ}^{+} and Y_G,

$$Z_{\xi}^{+} = (Y_G)^{\nu} = 0.57 \tag{8a}$$

The numerical value (0.57) for pure fluids differs from the corresponding value (0.48) obtained by field theory modelling [10]. This difference is due to the nonuniversal character of the reduction process of the physical quantities, which is always defined from an unknown density constant that depends on the choice of the length scale factor used to reduce in a nondimensional form the free energy per unit volume.

In a similar way, the dimensionless ordering field h^c along the critical isotherm is obtained as a nonasymptotic function ($h^c = Z_{D^c}(|m|)^{\delta}\,[1 + a_{h^c}(|m|)^{\Delta/\beta} + \cdots]$ with Z_{D^c} and a_{h^c} as constant amplitudes) of the dimensionless order parameter m, leading to the second relation between the numerical constants Z_{D^c} and F_G that reads

$$Z_{D^c} = (F_G)^{-\frac{3(\delta+1)}{2}} = 249 \tag{8b}$$

Provided that the reduction process uses the two characteristic length scale a_c and energy scale β_c for each pure fluid, the two numerical constants appearing in Eqs. (6a, 6b) (respectively, Eqs. (8a, 8b)) define the restricted universality of the one-component fluid subclass. Within this subclass, the linear scaling transformations (Eqs. (1a, 1b)) involve the use of the two phenomenogical scale factors Y_c and $(Z_c)^{-\frac{3}{2}}$ instead of Θ and Ψ, respectively.

3. COMPARISON WITH THE FITTING RESULTS OF THE CROSSOVER MODELS

Now, we are able to compare the results obtained using Eqs. (1a) to (8b) to the recent results [13–15] obtained for CO_2, CH_4, C_2H_4, C_2H_6, R134a, SF_6, and H_2O on the basis of the crossover description for the thermodynamic properties of critical fluids proposed by Albright et al. [13]. The Helmholtz free energy per unit volume is the free energy density selected as the critical potential. In this case, our characteristic parameter Y_c is identified as being the amplitude $-A_1$ of the linear term in the analytic expansion of the regular potential defined in Albright et al. analysis. Along the critical isochore, the dimensioned potential leading to the weak divergence of the specific heat is $\frac{P}{T}$, whose critical slope equals Y_c in its nondimensional form $\frac{P}{T}\frac{T_c}{P_c}$.

At the first-order of confluent correction to scaling for the Wegner expansion, the Albright et al. description uses scale dilatations equivalent to Eqs. (1a) and (5) [13–15]. In the asymptotic limit defined above and for symmetrical systems, only each first-order term of these scale dilatations is considered, that reads $t_A = c_t\, \Delta\tau^*$ and $m_A = c_\rho\, \Delta\rho^*$, respectively in Albright et al. notation. For higher order terms, the crossover description is more complex, precisely due to the inclusion of the crossover function from the critical region to the classical region, and also on account of the nonsymmetrical aspects of real fluids. In order to formulate this extension, it is necessary to add four characteristic nondimensional parameters, whose the relative importance is evaluated in the last part of this paper. Two of them are the *crossover* parameters, $\bar{u}$ and Λ in Albright et al. notation. $\bar{u}$ is related to the Φ^4-theory coupling constant u, which is rescaled by Λ^{4-d} in the Φ^4-term. Λ is an ultraviolet cutoff wave number. The scaled variable $\bar{u}$ reads $\bar{u} = \frac{u}{u^*}$, where u^* is the universal coupling constant of the RGT fixed point for three-dimensional Ising-like systems [15]. The other two terms are the *nonsymmetrical* parameters, c and d_1 in Albright et al. notation. c is a coefficient which determines the strength of the mixing of the field variables, while the coefficient d_1 represents a global asymmetry. As a first result, six parameters are free in the fitting procedure. Moreover, in order to keep the renormalized Helmholtz free energy finite at the critical point, and to obtain a correct classical free energy far away from the critical point, a suitable choice of the rescaling factors is needed. These factors are generally functions of the crossover parameters and the dimensionality of the system. Several published procedures differ in the renormalization schemes used and in the explicit consequences of the existence of a finite cutoff Λ for the critical fluctuations. In the Albright et al. procedure, the coupling between the six parameters in the fitted range including D_{AS} is not completely defined. As a final result, the universal ratios between leading amplitudes, and/or between the first confluent amplitudes for correction to scaling, do not exactly agree with more recent predictions of RGT [8], [16], and high-temperature expansions [9].

In light of the above discussion, the universal critical nature of this coupling can be revealed by fitting results, if the effective extension of the critical asymptotic domain is large enough to *recover* the self-consistency of the theory in the fitted range. To show this point, we need straightforward calculations of each respective *scale factor* ratios $\frac{Y_c}{c_t}$ and $\frac{(Z_c)^{1/2}}{c_\rho}$ as a function of the *crossover* product $\bar{u}\,\Lambda$ that gives the same estimates for the two independent asymptotic amplitudes $\frac{\xi_o^+}{a_c}$ and D^c, respectively (all the leading amplitudes being proportional to $(\bar{u}\,\Lambda)^{\Delta/\nu}$ in the Albright et al. crossover description). From trivial combinations of the results of Refs. 12 and 15, the calculated coupling functions are

$$\frac{Y_c}{c_t} = k_t (\bar{u}\,\Lambda)^{\frac{1}{\nu}-2} \tag{9a}$$

$$\frac{(Z_c)^{\frac{1}{2}}}{c_\rho} = k_\rho (\bar{u}\,\Lambda)^{\frac{\eta}{2}} \tag{9b}$$

η is another universal critical exponent associated to the density fluctuations at the critical point which is introduced here in order to close the hyperscaling between correlations and thermodynamics [16]. The prefactors k_t and k_ρ are then unequivocally related to the universal numerical values that are characteristic of the fluid-restricted universality [8],

$$k_t = \left[\frac{Z_\xi^+}{R_\xi^+ (R_\nu)^{-\frac{1}{d}}}\right]^{\frac{1}{\nu}} = 2.2748$$

$$k_\rho = \left[\frac{2(1+\eta)\, Z_{D^c}}{\left(\frac{u^*}{2}\right)^{\frac{2-\eta}{1+\eta}}}\right]^{\frac{d-2+\eta}{2d}} = 0.2127$$

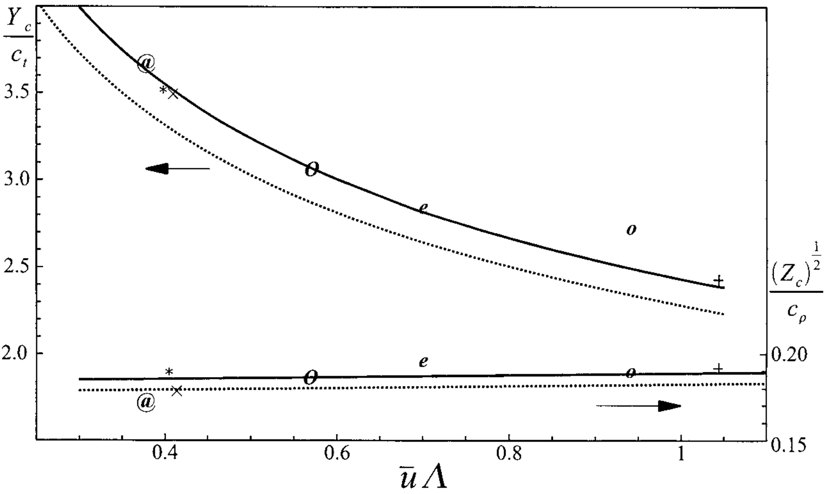

Fig. 1. Fluid scale-factor correlations as functions of $\bar{u}\Lambda$. Upper part / left axis: $\frac{Y_c}{c_t}$; Lower part / right axis: $\frac{(Z_c)^{1/2}}{c_\rho}$; Dashed curves: *exact* scale dilatation description (see text and Refs. 12 and 15); Full curves: *approximate* self-consistent crossover description (see text and Refs. 12, 14, and 15); Symbols: O CO_2; @ CH_4; o C_2H_4; × C_2H_6; + R134a; $*$ SF_6; and e H_2O (results of the crossover description for each fluid, see Refs. 13 and 14).

In the above equations, the values of the universal quantities ν, η, R_ξ^+, R_ν, and u^* are estimated from the *exact* RGT [8]. However, the small difference between pre-factors ($k_{tA} = 2.429$; $k_{\rho A} = 0.219$ obtained from Ref. 15) can be easily calculated also using the corresponding values obtained in the *approximate* crossover description [15]. Figure 1 illustrates the correlations for the exact (dotted curves) and approximate (full curves) cases.

We note a better agreement when the (approximate) consistency of the crossover description is allowed (see Fig. 1). This *self-consistent* agreement confirms the expected correlation between the *free* parameters in the fit and the *fixed* values of Y_c and Z_c. Note also that the crossover function has an explicit separation between the contributions to the leading amplitudes (proportional to $(\bar{u}\Lambda)^{\Delta/\nu}$) and to the first confluent amplitudes (proportional to $\bar{u}\Lambda(1-\bar{u})$) [15]. Then, the results reported in Fig. 1 are a clear confirmation that the first confluent correction terms to scaling are also governed by the same two asymptotic scale factors, as already demonstrated for xenon [10].

4. THE ASYMPTOTIC AND EFFECTIVE CRITICAL DOMAINS, AND THE CROSSOVER DOMAIN, IN THE TWO-PHASE RANGE

Now, we analyze the extension of D_{AS} into the two-phase domain. The pure fluid-restricted universality can be shown for the two-phase coexisting densities, ρ_{L} (liquid) and ρ_{V} (vapour), expressing $m_{\mathrm{LV}} \times (-t)^{-\beta}$ as a function of $-t$ from Eqs. (1a) to (5), without any adjustable parameter. $m_{\mathrm{LV}} = (Z_c)^{\frac{3}{2}} \Delta n^*_{\mathrm{LV}} = (Z_c)^{\frac{1}{2}} \Delta\rho^*_{\mathrm{LV}}$ is the dilated order parameter for the two-phase range, where $\Delta n^*_{\mathrm{LV}} = \frac{n_L - n_V}{2n_c}$ and $\Delta\rho^*_{\mathrm{LV}} = \frac{\rho_L - \rho_V}{2\rho_c}$. It is currently admitted that $\Delta\rho^*_{\mathrm{LV}}$ is the *symmetrical* form of the order parameter for the one-component fluids. Figure 2 shows the results for selected pure fluids where we have used the density difference values $\rho_{\mathrm{L}} - \rho_{\mathrm{V}}$, published in table data of the literature as *rough* entry values.

The comparison between, (a) the range $-t > 2 \times 10^{-1}$, where significant differences are observed for the behavior of the dilated forms of the coexistence curve near the triple point, and (b) the asymptotic domain $-t \leqslant 10^{-3}$ close to the critical point, enhances the universal asymptotic

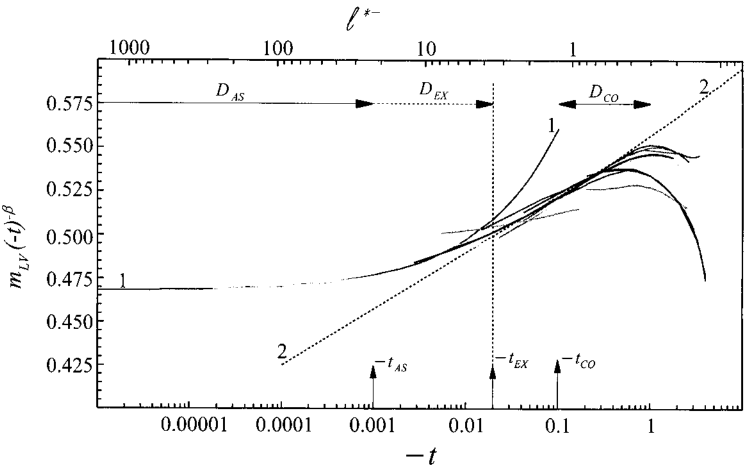

Fig. 2. $m_{\mathrm{LV}}\,(-t)^{-\beta}$ as a function of $-t$ (lower log-axis) or as a function of $\ell^{*-} = \frac{\xi^-}{a_c} = Z_\xi^-(-t)^{-\nu}\,[1 + a_\xi^-(-t)^{\Delta}]$ [17] (upper log-axis); Full curve 1: first-order Wegner expansion ($m_{\mathrm{LV}} = Z_M^-\,(-t)^{\beta}\,[1 + a_M^-\,(-t)^{\Delta}]$, see text and Ref. 17); Dotted curve 2: effective power law ($m_{\mathrm{LV}} = 0.563\,(-t)^{0.355}$, see text and Ref. 18); Others curves: experimental results for CO_2; CH_4; C_2H_4; C_2H_6; R134a; SF_6; and H_2O (see references cited on Refs. 13 and 14). Arrows and associated labels: D_{AS} is the asymptotic critical domain covering the range $-t \lesssim -t_{\mathrm{AS}}$, with $-t_{\mathrm{AS}} \simeq 10^{-3}$; D_{EX} is the extended critical domain covering the range $-t \lesssim -t_{\mathrm{EX}}$, with $-t_{\mathrm{EX}} \simeq 2 \times 10^{-2}$; D_{CO} corresponds to the crossover in the range $-t_{\mathrm{CO}} \gtrsim -t \gtrsim -10 \times t_{\mathrm{CO}}$, with $-t_{\mathrm{CO}} \simeq 10^{-1}$; (see also the text).

character of their singular behavior when $-t$ goes to zero. The same pure fluid-restricted universality is shown close to the critical point whatever the nature (gas or liquid) of the coexisting phases. This observation can be easily made using $\Delta\rho^{*+} = (\frac{\rho_L}{\rho_c}) - 1$ (liquid branch), and $\Delta\rho^{*-} = 1 - (\frac{\rho_V}{\rho_c})$ (vapor branch) in addition to $\Delta\rho^{*}_{\mathrm{LV}}$. This result confirms that the fluid-restricted Wegner expansion limited to the first order $m_{\mathrm{LV}} = Z_M^- (-t)^{\beta} [1 + a_M^- (-t)^{\Delta}]$ [17] (see the full curve 1 in Fig. 2) is completely specified by the two-scale-factors (Eqs. (4)). Taking into account the relation between the nondimensional correlation length ℓ^{*-} and $-t$ along the critical isochore below T_c, the upper axis in Fig. 2 can be directly labelled in units of $\ell^{*-} = \frac{\xi^-}{a_c} = Z_\xi^- (-t)^{-\nu} [1 + a_\xi^- (-t)^{\Delta}]$ [17]. This latter expression, limited to first order of the fluid-restricted Wegner expansion, describes the scaling behavior of the correlation length in the coexisting two-phase range ($t < 0$), as Eq. (7) describes the one in the one-phase range ($t > 0$). For $-t \leqslant -t_{\mathrm{AS}} \cong 10^{-3}$, $\ell^{*-} \geqslant 30$. So that, inside this domain, now defined as being the asymptotic critical domain D_{AS} for the one-component fluids, the typical size of the critical fluctuations is always larger than the range of the molecular interactions.

In Figure 2, another interesting feature is revealed by the dotted curve 2 of *effective* master equation $m_{\mathrm{LV}} = Z_{\mathrm{eff}} (-t)^{\beta_{\mathrm{eff}}}$, where $Z_{\mathrm{eff}} = 0.557$ and $\beta_{\mathrm{eff}} = 0.355$. This curve suggests a quasi-universal behavior in the limited intermediate range $10^{-2} < -t < 7 \times 10^{-2}$, that is *outside* the asymptotic domain of validity for the Wegner expansion limited to first order. As a matter of fact, using the above power law with effective exponent, we are able to recover all the previous descriptions of the gas-liquid coexistence curves based on the scaled equations of state which have used $\beta_{\mathrm{eff}} = 0.355$ [18]. In addition to this quasi-universal behavior, we note that the critical correlation length always remains 3 or 4 times larger than the range of the molecular interactions for $-t < -t_{\mathrm{EX}} \cong 2 \times 10^{-2}$. So that, we propose *one more decade* extension ($\ell^{*-} \geqslant 3$) of the critical domain, noted now D_{EX}, up to the upper limit $-t_{\mathrm{EX}}$. Inside D_{EX}, master scaling behavior expressed in terms of the appropriate dilated two-phase variables are expected, whatever the one-component fluid, as illustrated in Fig. 2 for the rescaled order parameter case. In this extended domain, the fluid-restricted universality is described only by the two asymptotic scale factors defined by Eqs. (1a) and (1b). The functional form of the rescaled master behavior is still an open problem due to the implicit coupling between the poor knowledge of higher-order terms of the Wegner expansion and the complex functional form of the global crossover description, as mentionned above. Moreover, the non-symmetrical form of the liquid-gas coexistence curve appears to have a main influence outside D_{AS}. Nevertheless its lowest order resulting contribution to the symmetrical form seems sufficiently small in the extended domain D_{EX} to avoid the introduction of a new characteristic parameter, except for the slope of the rectilinear density diameter observed precisely in this intermediate range.

In order to show now the appearance of the crossover with a minimization of the spurious effects due to the correlations between amplitudes and exponents of the complementary Wegner expansion-like terms, we have reported in Fig. 3 the behavior of the effective exponent $\beta_{\mathrm{eff}} = \frac{d[\mathrm{Ln}(\Delta\rho^{*}_{\mathrm{LV}})]}{d[\mathrm{Ln}(-\Delta\tau^{*})]}$ as a function of $-\Delta\tau^{*}$ for (the standard fluid) xenon using extensive literature results [19–11]. The characteristic parameter $Y_{c(\mathrm{Xe})} = 4.9$ [11] of the standard fluid gives the dilated universal scale $t = Y_{c(\mathrm{Xe})}\,\Delta\tau^{*}$ reported on the upper axis of this Fig. 3, that corresponds to the lower axis of Fig. 2. This abscissa link between Figs. 2 and 3 allows the analysis using the temperature distance to $T_{c(\mathrm{Xe})} = 289.74\ K$, as well as the dilated scaling field $-t$. The curve 1 in Fig. 3 corresponds to the first-order Wegner expansion $\beta_{\mathrm{eff}} = \beta[1 + \frac{\Delta}{\beta}\, a^{(1)}_{B(\mathrm{Xe})}(-\Delta\tau^{*})^{\Delta}]$, where $a^{-}_{M} = \frac{a^{(1)}_{B(\mathrm{Xe})}}{[Y_{c(\mathrm{Xe})}]^{\Delta}}$ [17], with $a^{(1)}_{B(\mathrm{Xe})} = 1.4$ [11]. The curves 2 to 8 correspond to the literature results (see details in Ref. 19). The length of each curve 2 to 8 indicates the respective experimental temperature ranges, (a) when a constant value for the

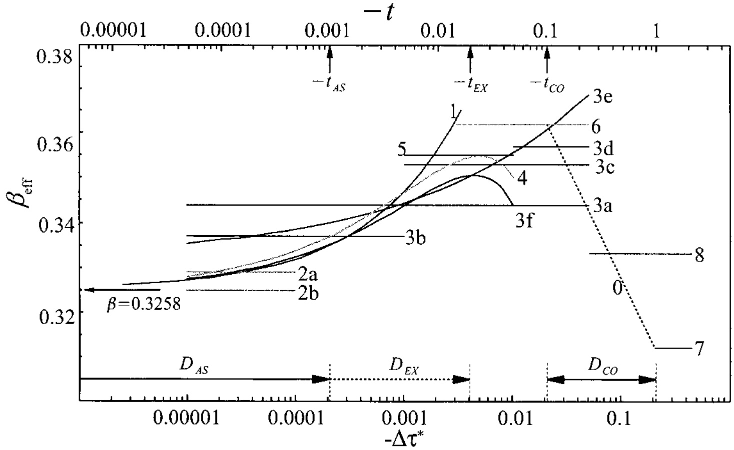

Fig. 3. β_{eff} for xenon as a function of $-\Delta\tau^{*}$ (lower log-axis) or as a function of $-t$ (upper log-axis); Curve 1: from the first-order Wegner expansion ($\beta_{\mathrm{eff}} = \beta[1 + \frac{\Delta}{\beta}\, a^{(1)}_{B(\mathrm{Xe})}(-\Delta\tau^{*})^{\Delta}]$, see Ref. 17, with $\beta = 0.3258$, $\Delta = 0.5$, and $a^{(1)}_{B(\mathrm{Xe})} = 1.4$ [11]); Lines 2 to 8 are from the literature results (see Ref. 19 for details). The length of each curve indicates the covered experimental temperature ranges (see text); Line 0 is a guide to show the crossover link between the highest *plateau* value ($\approx 0.36-0.37$) and the lowest value ($\approx 0.31-0.32$) of β_{eff} far from the critical point. The arrows and the associated labels D_{AS}, D_{EX}, D_{CO}, $-t_{\mathrm{AS}}$, $-t_{\mathrm{EX}}$, and $-t_{\mathrm{CO}}$ are defined in the caption of Fig. 2 (see also the text).

effective exponent is observed (straigth lines, using the power law $\Delta\rho^*_{\mathrm{LV}} = B_{\mathrm{eff}}\,(-\Delta\tau^*)^{\beta_{\mathrm{eff}}}$ to fit the data with B_{eff} and β_{eff} as free parameters) and (b) when the fitting was performed in terms of the correction-to-scaling form of the Wegner expansion (curved lines). So that, away from the critical point, the departures of the literature curves from curve 1 reflect the relative global contribution of the complementary effects discussed above. The resulting characteristic behavior of β_{eff} associated to the nonasymptotic crossover is then well-emphasized by the line 0 crossing the value $\ell^{*-} \approx 1$. We note that the line 0 is only a guide to show the functional link between the highest *plateau* value ($\approx 0.36-0.37$) and the lowest value ($\approx 0.31-0.32$) of β_{eff} far from the critical point. This heuristic method is appropriate to define the scaling field decade $-t_{\mathrm{CO}} \leqslant -t \leqslant -10 \times t_{\mathrm{CO}}$, which starts at $-t_{\mathrm{CO}} \cong 10^{-1}$, as being the range where the crossover from the nonclassical behavior close to the critical point, to the mean-field behavior further away from the critical point occurs.

5. CONCLUSION

From the present analyses of the results shown in Figs. 2 and 3, we note three conclusive remarks. (a) For xenon, the extension of D_{AS}, corresponding to the first-order Wegner expansion, is no more valid for $-\Delta\tau^* \geqslant 2\times 10^{-4}$ (or $(T_c - T)_{\mathrm{Xe}} \geqslant 60$ *mK*). Within this asymptotic critical domain where $\frac{\xi^-}{a_c} \gtrsim 30$, (or $-t \lesssim -t_{\mathrm{AS}}$, see the corresponding arrows in Figs. 2 and 3), *all* the pure fluids can be considered as *ideal* critical fluids showing a *one-component fluid-restricted universality* similar to the one predicted from the *symmetrical* one-component Φ^4 model, except for a minor numerical adjustment [11, 16]. (b) Our extended critical domain D_{EX} is valid up to a reduced temperature distance $-\Delta\tau^* \approx 3-4\times 10^{-3}$ for xenon (or $(T_c - T)_{\mathrm{Xe}} \approx 1$ *K*). The typical values $\frac{\xi^-}{a_c} \gtrapprox 3$ (or $-t \lesssim -t_{\mathrm{EX}}$, see the corresponding arrows in Figs. 2 and 3) can be considered as a common lower limit in the case of the eigth selected pure fluids. (c) For xenon, the *non-asymptotic* crossover is demonstrated to be in the range D_{CO} where $-\Delta\tau^* \geqslant 2\times 10^{-2}$ (the curve 0 corresponds to the temperature range 6 $K \lesssim (T_c - T)_{\mathrm{Xe}} \lesssim 60$ *K*). In that case, $\frac{\xi^-}{a_c} \lessapprox 1$ (or $-t \gtrsim -t_{\mathrm{CO}}$, see the corresponding arrows on Figs. 2 and 3). In light of the present work, its seems now suitable to revisit the description of the nonsymmetrical and nonasymptotic crossover characteristics of each pure fluid. As a special mention related to the above purpose, we note the significant microscopic differences between the gas-like and the liquid-like non-zero values of the order parameter or the ordering field which, after crossover, permit to recover the *perfect gas* description of the fluid at low-density (on the gas side) or the complex multiparameter description of the condensed matter (on the liquid side).

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17. Rescaled amplitude values leading to the fluid-restricted universality; $Z_\chi^+=0.12$; $Z_M^-=0.468$; with $Z_\chi^+\,Z_{D^c}\,(Z_M^-)^{\delta-1}=R_\chi^+$; $\frac{Z_\xi^+}{Z_\xi^-}=1.96$; $\frac{a_\xi^+}{a_\chi^+}=0.65$; $\frac{a_\chi^+}{a_M^-}=0.9$; $\frac{a_\xi^+}{a_\xi^-}=1$; $a_M^-=0.63$ ($a_\chi^+=0.7$ see Ref. 11); $a_\xi^-=0.45$ ($a_\xi^+=0.45$, see Ref. 11).
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