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We discuss a phenomenological method which allows to determine the singular asymptotic behaviours for a pure fluid at equilibrium, when the liquid-gas critical point and the tangent plane to the characteristic surface of this point are localized experimentally, in the pressure, density and temperature coordinates.

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I. INTRODUCTION

The renormalization group (RG) theory has contributed to the description of the critical phenomena observed in systems at equilibrium very close to their second order transition points where the order parameter of the transition goes to zero continuously [1]. Very different physical systems can be grouped within the same universality class [1, 2] if they have the same dimension d of the space, and the same dimension n of the order parameter (OP) density, respectively. For each given class, the RG theory predicts the existence of two dimensionless parameters characteristic of each system belonging to this class [1, 3, 4, 5, 6]. This result is a verification of the two-scale factor universality hypothesis [7]. However, the theory is unable to provide values for these two parameters which are system-dependent.

In the present study, we propose a phenomenological determination of these two characteristic parameters for a pure fluid at equilibrium very close to its gas-liquid critical point (CP). We demonstrate that the asymptotic singular behaviour of such near-critical fluid can be completely defined by four different critical parameters which are: i) the critical pressure, p_c; ii) the critical temperature, T_c; iii) the critical density, ρ_c; iv) the common limiting critical slope, $\gamma_c^{'}$, in the p,T diagram, of the saturation vapor pressure curve and the critical isochore at the critical point. As a result, the two scale factors characteristic of each pure fluid can be related to these four quantities.

In order to derive the explicit forms of the two scale factors, we select the two asymptotic amplitudes, ξ^+ and D^c as being the two independent (but each one system-dependent) parameters. ξ^+ is the asymptotic amplitude for the dimensionless correlation length, ℓ^*, along the critical isochore in the single phase region. D^c is the amplitude for the dimensionless chemical potential difference, $\Delta\mu^*_{\bar{p}} = \mu^*_{\bar{p}} - \mu^*_{\bar{p},c}$, along the critical isotherm (here the chemical potential refers to the normalized thermodynamics per particle). All the pure fluids constitute a sub-class within the universality class $d = 3$ and $n = 1$ [8, 9], for which the asymptotic behaviour is then completely determined provided that the same definitions for dimensionless quantities can be used for any pure fluid. Therefore, we also propose in this study an explicit selection of the two macroscopic parameters of energy dimension and length dimension, respectively, which are necessary to formulate a description of the critical phenomena observed close to the CP in terms of the dimensionless variables.

In the next section 2, we recall the main results of the RG theory for $d = 3$ and $n = 1$ which are needed for a correct description (in terms of ξ^+ and D^c) of the universal features of the critical behavior for the pure fluid subclass. In section 3, we unequivocally define four different quantities characteristic of pure fluids in terms of T_c, p_c, ρ_c and $\gamma_c^{'}$. Then we introduce $(\beta_c)^{-1} = k_B T_c$ and $\alpha_c = \left(\frac{k_B T_c}{p_c}\right)^{\frac{1}{d}}$ (k_B is the Boltzmann's constant), as units of length and energy, respectively, to made dimensionless all the thermodynamics properties and correlations functions. The remaining two dimensionless parameters are $Y_c = \gamma_c^{'}\frac{T_c}{p_c} - 1$ and $Z_c = \frac{p_c m_{\bar{p}}}{\rho_c k_B T_c}$ ($m_{\bar{p}}$ is the molecular mass of the fluid particle). In section 4, we give relations which enable the unequivocal calculation of the amplitudes, ξ^+ and D^c, knowing Y_c and Z_c. The agreement with the existing experimental data is very good. Using these relations, we propose in section 5, a scale dilatation method of the physical fields which provide a formulation of the asymptotic universality for the pure fluid subclass equivalent to the one obtained from the RG methods applied to the complete universality class. For crossing CP along the thermodynamic path corresponding to the critical isochore, this formulation uses quantities such as pressure and temperature which are directly accessible with experiments. We conclude after a qualitative comparison to the recent results of Bagnuls and Bervillier [10] given in section 6.

II. RECALL OF THE MAIN RESULTS OBTAINED FROM RG THEORY

The theoretical results will be concerned with systems (noted S) belonging to the universality class, $d = 3$ and $n = 1$. Our presentation will be limited to the characterization of the asymptotic singular behavior of a property, X_S, which is expected to follow the non-analytic power-law

$$X = X_S^{(L)} \left(\tau_S^*\right)^{-x} \left[1 + \mathcal{O}\left(\tau_S^*\right)\right] \tag{1}$$

when τ_S^* goes to zero. All the quantities which appear in Eq. (1) are made dimensionless (see below). τ_S^* is a small finite physical field, associated to a thermodynamic path denoted by the subscript (L), which vanishes asymptotically to CP ($\tau_S^* = 0$ at CP). When the subscript (L) denote the *critical isochore* of S, the associated field τ_S^* can be thus defined as the *thermal* field, $\tau_S^* \equiv \Delta\tau^* = \frac{T-T_c}{T_c}$, which is the dimensionless temperature distance to CP for fluid systems. Along this critical isochore, (L) will be then noted + when the critical point is approached from the single phase region ($T > T_c; \Delta\tau^* > 0$) and - when the critical point is approached from the two-phase region ($T < T_c; \Delta\tau^* < 0$). The exponent x is a universal number which depends not on the system, but on the universality class that the system belongs to. The reduced asymptotic amplitude, $X_S^{(L)}$ is a system dependent quantity. The term $\left[1 + \mathcal{O}\left(\tau_S^*\right)\right]$ corresponds to the so-called Wegner expansion [11], which accounts for the deviation from power-law behaviour with increasing τ_S^* due to the confluent corrections to scaling. Such a corrective expansion will not be taken into consideration in this study [12]. Similar power law formulations of the singular behaviors of X_S can be provided in terms of the vanishing *ordering* field, hereafter noted h_S^* (with $h_S^* = 0$ at CP), when the thermodynamic path to cross CP corresponds to the critical isotherm (with $(L) \equiv c$ in that case).

For any system S belonging to the universality class $d = 3$ and $n = 1$, noted $\phi^4_{d=3}(1)$ in the following, the RG numerical results obtained from the non linear treatment of ϕ^4 model in three dimensions [3, 4, 5], are of sufficient accuracy to verify the two-scale factor universality hypothesis. Therefore, there are only ten universal relations between the twelve asymptotic amplitudes as there are only ten scaling laws related to twelve critical exponents [13]. As a result, the non-universality of $\phi^4_{d=3}(1)$, can be adequately characterized by selection of two independent asymptotic amplitudes. In this present study, we chose the two amplitudes, ξ^+ and D^c, defined as follows:

i) along the critical isochore in the single phase region ($\tau_S^* > 0$; $h_S^* = 0$; $(L) \equiv +$)

$$\ell_S = \xi^+ \left(\tau_S^*\right)^{-\nu} \tag{2}$$

ii) along the critical isotherm ($\tau_S^* = 0$; $h_S^* \neq 0$; $(L) \equiv c$)

$$h_S^* = D^c \left|m_S^*\right|^{\delta} \tag{3}$$

where ν and δ are the two critical exponents of respective universal value. m_S^* is the order parameter (OP) density for the transition, while h_S^* is it congugate ordering field. ℓ_S^* is the correlation length of the OP density fluctuations. For the case where S is a one-component fluid in the close vicinity to its CP, (with the fluid subclass noted $VLCP$ in the following), OP density is proportional to the difference between the *number* density ($n = \frac{N}{V} = \frac{\rho}{m_{\bar{p}}}$) and the critical number density ($n_c = \frac{\rho_c}{m_{\bar{p}}}$), i.e. $m_S^* \equiv \Delta n^* \propto \Delta n = n - n_c = \frac{\Delta\rho}{m_{\bar{p}}} = \frac{\rho-\rho_c}{m_{\bar{p}}}$ (N is the total amount of matter, i.e. the total number of constitutive particles, and V is the total volume of the system). Its conjugate *ordering* field is then proportional to the difference between the chemical potential per particle ($\mu_{\bar{p}} = \mu_\rho \times m_{\bar{p}}$) and the critical chemical potential ($\mu_{\bar{p},c} = \mu_c \times m_{\bar{p}}$), i.e. $h_S^* \equiv \Delta\mu_{\bar{p}}^* \propto \Delta\mu_{\bar{p}} = \mu_{\bar{p}} - \mu_{\bar{p},c} = \Delta\mu \times m_{\bar{p}} = (\mu_\rho - \mu_{\rho,c}) \times m_{\bar{p}}$. We note that the *mass* density ρ and the chemical potential per mass unit μ_ρ are the two conjugated density-field variables when the thermodynamics is normalized per mass unit [14].

In Table 1, we present the results of RG treatment where we can easily verify that the two numbers, ξ^+ and D^c are sufficient for complete calculation of all the other asymptotic amplitudes [15]. The estimated values of the two independent exponents, ν and δ, are 0.63 and 4.815, respectively [4].

We emphasize however that this RG formulation of universal features for any complete class is only the consequence of the basic assumptions in this theoretical approach [16]. Indeed, this approach assumes analytical relations between the two relevant renormalized fields, t^* and h^*, of the model, and the corresponding physical fields, τ_S^* and h_S^*, of the system. In the asymptotic near critical domain, these relations are given by

$$t^* = \vartheta\tau_S^* + \mathcal{O}\left[\left(\tau_S^*\right)^2, \tau_S^* h_S^*\right] \tag{4}$$

$$h^* = \psi h_S^* + \mathcal{O}\left[\left(h_S^*\right)^2, \tau_S^* h_S^*\right] \tag{5}$$

where the scale factors ϑ and ψ are mandatory system-dependent parameters. The concept of two-scale factor universality lies behind the direct linearization of equations (4) and (5) [10, 16], according to which each system is characterized uniquely by the two factors, ϑ and ψ, linked to τ_S^* and h_S^*, respectively [10, 16]. It is therefore equivalent to characterize the non-universality of the fluid, either by two independent amplitudes, such as ξ^+ and D^c, or by the two scale factors, ϑ and ψ [17].

a. Universality class		Amplitudes	Amplitude combinations	Exponents	Scaling laws
Thermodynamics & Correlations	Independent quantities	ξ^+ D^c		$\nu = 0.63$ $\delta = 4.815$	
	Universality	$A+$ $\hat{D}$	$R_\xi^+ = \xi^+ \left(A^+\right)^{\frac{1}{d}}$ $R_D = D^c \left(\hat{D}\right)^{\frac{\delta+1}{2}}$	α η	$d\nu = 2 - \alpha$ $\frac{2-\eta}{d} = \frac{\delta-1}{\delta+1}$
Thermodynamics	Independent quantities	$D^c,\ A^+$		$\delta,\ \alpha$	
	Universality	Γ^c A^c Γ^+ B Γ^- A^-	$l = \delta\Gamma^c \left(D^c\right)^{\frac{1}{\delta}}$ $Q_{A^c} = A^c \left[\delta A^+ \left(D^c\right)^{\frac{1}{\delta}}\right]^{\frac{-\alpha}{2-\alpha}}$ $Q_{\Gamma^+} = \left(\Gamma^+\right)^{\frac{\delta+1}{\delta}} \left[\left(A^+\right)^{\delta-1} \left(D^c\right)^2\right]^{\frac{1}{\delta}}$ $Q_B = B \left(\frac{D^c}{A^+}\right)^{\frac{1}{\delta+1}}$ Γ^+/Γ^- A^+/A^-	γ^c α^c γ β $\gamma^{'}$ $\alpha^{'}$	$\gamma^c = \frac{\delta-1}{\delta}$ $\alpha^c = \frac{\alpha(\delta+1)}{2-\alpha}$ $\gamma = \frac{(2-\alpha)\cdot(\delta-1)}{\delta+1}$ $\beta = \frac{2-\alpha}{\delta+1}$ $\gamma = \gamma^{'}$ $\alpha = \alpha^{'}$
Correlations	Independent quantities	$\xi^+,\ \hat{D}$		$\nu,\ \eta$	
	Universality	ξ^c ξ^-	$Q_{\xi^c} = \xi^c \left(\hat{D}\right)^{\frac{\delta+1}{2d\delta}}$ ξ^+/ξ^-	ν^c $\nu^{'}$	$\nu^c = 2/\left(d+2-\eta\right)$ $\nu = \nu^{'}$

b. relations to the amplitude combinations defined in Table 1 of reference [13]		
$Q_{A^c} = \left[R_{A^c}/\left(R_{\xi^+}\right)^{2d}\right]^{-\alpha/(2-\alpha)}$ $Q_{\Gamma^+} = \left[\left(R_\chi\right)^2 \left(R_C\right)^{\delta-1}\right]^{1/\delta}$ $Q_B = \left(R_\chi/R_C\right)^{1/(\delta+1)}$ $Q_{\xi^c} = \left[Q_2 Q_3/\delta \left(R_D\right)^{1/\delta}\right]^{2\delta/(\delta-1)}$	$\left\{\begin{array}{l} R_\xi = \Gamma^+ D B^{\delta-1} \\ R_C = A^+\Gamma^+/B^2 \\ R_{A^c} = \left[\left(\xi^+\right)^2 \left(A^c\right)^\nu\right]^d \left(\Gamma^c\right)^\alpha \end{array}\right.$	$\left\{\begin{array}{l} Q_1 = \Gamma^c\delta\left(B^{\delta-1}\Gamma^+\right)^{-1/\delta} \\ Q_2 = \left(\Gamma^+/\Gamma^-\right)\left(\xi^c/\xi\right)^{2-\eta} \\ Q_3 = \hat{D}\left(\xi^+\right)^{2-\eta}/\Gamma^+ \end{array}\right.$

Table I: a. Equivalence between the ten universal amplitude combinations and the ten scaling laws connecting the twelve asymptotic amplitudes and the twelve critical exponents, respectively, for the universality class $d = 3$ and $n = 1$. The definitions and notations are those used in Ref. [13], except for the four new universal ratios Q_{A^c}, Q_{Γ^+}, Q_B (which have been introduced in the "Thermodynamics" part), and Q_{ξ^c} (which have been introduced in the "Correlations" part) of this Table. Of course, they are connected to the other universal ratios proposed in Ref. [13], as shown in the lower part b. In part a, each mixed description and each separated description of the thermodynamic properties and the correlation functions are made in terms of the two amplitude-exponent pairs selected as being independent.

III. CHARACTERISTIC PARAMETERS OF VLCP

The singular thermodynamic properties of a pure fluid are usually expressed in reduced form using T_c, p_c and ρ_c [18]. Such a procedure, however presents difficulties [19]. The results are often given in terms of the critical compression factor Z_c which is defined by the relation

$$Z_c = \frac{p_c m_{\bar{p}}}{\rho_c k_B T_c} \tag{6}$$

and which is a characteristic parameter of each pure fluid. Moreover, the knowledege of the three critical parameters, T_c, p_c and ρ_c is not suficient to define the thermodynamic paths of crossing CP. Indeed, the definition of these lines require not only to localise the critical point in the phase space, but also to provide the position of the tangent plane with respect to the phase surface at this point. To precise that topological aspect, we consider the phase surface of equation $f(p, \rho, T) = 0$ used by the experimentalists, which results from the equation of state $p(v_{\bar{p}}, T) = -\left(\frac{\partial a_{\bar{p}}}{\partial v_{\bar{p}}}\right)_T$, where $a_{\bar{p}}(T, v_{\bar{p}})$ is the Helmoltz energy per particle, and $v_{\bar{p}} = \frac{1}{n} = \frac{m_{\bar{p}}}{\rho}$ is the volume per particle (considering here a one-component fluid at constant amount of matter and the thermodynamic potentials normalized per particle, such as for example $a_{\bar{p}}(T, v_{\bar{p}}) = \frac{A(T,V,N)}{N}$, where $A(T, V, N)$ is the total Helmoltz free energy).

The tangent plane to this phase surface at CP is defined by two orthogonal lines which pass through CP. One direction is trivial - parallel to the axis of the normalized extensive variable $v_{\bar{p}}$ - and is common to all the fluids (reflecting infinite value of their isothermal susceptibility at CP). On the contrary, the second (finite) direction is characteristic of each pure fluid. It is defined as the common limiting slope $\gamma_c^{'}$ at the critical point, in the $p;T$ diagram, of the saturation vapor pressure curve $p_{sat}(T)$ and of the *isochoric* pressure $p(T,\rho_c)$ along the critical isochore. $\gamma_c^{'}$ can be expressed as

$$\gamma_c^{'} = \frac{\partial}{\partial T}\left[p(T,\rho_c)\right]_{T\to T_c^+} = \frac{d}{dT}\left[p_{sat}(T)\right]_{T\to T_c^-} \qquad (7)$$

In view of the thermodynamic approach to CP, there are four macroscopic critical parameters. We unambiguously define four new quantities given by the following equations [19]

$$(\beta_c)^{-1} = k_B T_c \qquad (8)$$

$$\alpha_c = \left(\frac{k_B T_c}{p_c}\right)^{\frac{1}{d}} \qquad (9)$$

$$Z_c = \frac{p_c m_{\bar{p}}}{\rho_c k_B T_c} \qquad (10)$$

$$Y_c = \gamma_c^{'}\frac{T_c}{p_c} - 1 \qquad (11)$$

where $(\beta_c)^{-1}$ and α_c are two quantities evaluated at the CP, with dimensions of energy and length, respectively. They are sufficient to reduce the physical quantities of fluids into their dimensionless form [20]. Z_c and Y_c are then two dimensionless parameters, characteristics of each fluid.

The analyses of the thermodynamic analogies between systems belonging to the same universality class [8, 9] are at the origin of the relations (10) and (11). These analogies establish the symmetry properties of the characteristics surfaces [9]. For the case of pure fluids along the critical isochore in the single phase domain, the normalized field $\frac{p}{T}$ seems thus the analog of the density of the total Gibbs free energy for the case of Ising systems belonging to $\phi^4_{d=3}(1)$ (considering then the system maintained at constant volume and the thermodynamics normalized per volume unit) [21, 22]. The definition of α_c, such as a length unit of Eq. (9), arises from the natural reduction of $\frac{p}{T}$ by the corresponding critical intensive parameters (which are then non-dependent of the total volume of the system). The fact that the asymptotic divergence of the specific heat at constant volume along this path is only due to the contribution of the singular part of $\frac{p}{T}$, is also taken into account in establishing the dimensionless form of Y_c given by Eq. (11) [21, 23].

We emphasize that the dimensionless numbers Z_c and Y_c are not two of the twelve dimensionless asymptotic amplitudes of $\phi^4_{d=3}(1)$ which are defined in Table 1.

All the pure fluids should show universal behavior predicted by RG methods is an introductive hypothesis given in the present work. Consequently, we admit that ξ^+ and D^c are related to Z_c and Y_c by both functional forms given below

$$\xi^+ = \xi^+(Y_c, Z_c) \qquad (12)$$

$$D^c = D^c(Y_c, Z_c) \qquad (13)$$

It stands out that this new formulation of our hypothesis has an important topological characteristic. The functional relations (12) and (13) assume that all the information necessary to describe the asymptotic behavior in approaching the CP is contained in the location of this point at the characteristic surface and the tangent plane to this surface at this point.

IV. PHENOMENOLOGICAL DETERMINATION OF ξ^+AND D^c

The selection of the amplitudes, ξ^+ and D^c, indicates two paths of thermodynamic approach which are distinct in their thermodynamic nature. One path is on the critical isochore (a line for a fluid at *constant extensivity*) and the other path is on the critical isotherm (a line for a fluid at *constant intensivity*).

Equations (12) and (13) can be simplified if each asymptotic amplitude is only a function of one of the factors. Y_c should be for the critical isochore since it is the reduced form of the slope of the potential $\frac{p}{k_B T}$ along this path. To establish a connection between Z_c and the critical isotherm, we need to resort to the results of GR which show that the amplitude D^c is related to the amplitude $\widehat{D}$ through the universal ratio $R_D = D^c\left(\widehat{D}\right)^{\frac{\delta+1}{2}}$ (see Table I). Since $\widehat{D}$ has one divergent quantity at the *exact critical point* ($t^* = 0; h^* = 0$), Z_c and $\widehat{D}$ are the only parameters defined uniquely at the *exact criticality.* Therefore, it is legitimate to associate the Z_c specific role to the critical isotherm since the direction of the tangent plane along this line is also defined by this same parameter, for every pure fluid. We lay down therefore the importance of these phenomenological observations to introduce two supplementary hypotheses.

i) *The dimensionless number Y_c is characteristic of only the singular asymptotic domain along the critical isochore.*

ii) *The dimensionless number Z_c is characteristic of only the singular asymptotic domain along the critical isotherm.*

Thus, the above functional forms (12) and (13) can be modified as follows:

$$\xi^+ = \xi^+(Y_c) \qquad (14)$$

$$D^c = D^c(Z_c) \qquad (15)$$

The phenomenological arguements which permit to explicit the above functional forms will be provided in a more detailled manner in the following sections. However, for practical (critical) dimensional analysis, the above functional forms (14) and (15) can be already written as the following equations

$$\xi^{+}\left(Y_c\right)^{\phi}=Y_G \tag{16}$$

$$D^c\left(Z_c\right)^{\zeta}=F_G \tag{17}$$

where we expect that ϕ, ζ, Y_G and F_G have the same values for all pure fluids. Since the experimental values of Z_c and Y_c are available for a large number of fluids, there are six unknown quantities in equations (16) and (17).

For the determination of the above unknown parameters ϕ, ζ, Y_G and F_G, it is in principle sufficient to know the experimental values for ξ^{+} and D^c for only two fluids with different Z_c and Y_c values. We emphasize that the asymptotic nature of the amplitudes ξ^{+} and D^c imposes that experiments to be performed in the region as close as possible to CP, with high relative accuracy [14], particulary in order to minimize the contribution of the corrective terms [24] in the Wegner expansion.

The previous conditions are partly realized in the Franhauffer diffraction experiments [25], and in some light scattering experiments [26, 27, 28, 29], for the three fluids Xe, SF_6, and CO_2. However, the amplitude D^c, which can only be deduced from the results of the diffraction experiments, remains determined with a large uncertainty, reflecting the impossibility to observe directly the critical shape of the critical isotherm for the chemical potential of a pure fluid [30].

This is why it would be preferable to find another way which would enable the calculation of D^c, avoiding the difficulties mentioned previously, but maintaining always enable the unequivocal determination of ϕ, ζ, Y_G and F_G. Indeed, the values of the three amplitudes ξ^{+}, Γ^{+} and B, where any two of which are independent, can be obtained with acceptable precision from experiments. Γ^{+} is the amplitude for the power law divergence of the susceptibility along the critical isochore in the single phase domain and B is the amplitude of the power law top-shape of the vapor-liquid coexistence curve in the two phase domain. We can thus utilize the theoretical universal value of the amplitude combination R_{χ} (see Table I) to obtain D^c knowing Γ^{+} and B. More generally, starting with the experimental values for any amplitude pair made from the three amplitudes ξ^{+}, Γ^{+} and B, the remaining non-selected amplitude and D^c can be calculated from the following universal amplitude combinations (see Table I)

$$R=R_{\xi}^{+}\left(R_C\right)^{-\frac{1}{d}}=\xi^{+}\left(\frac{B^2}{\Gamma^{+}}\right)^{\frac{1}{d}} \tag{18}$$

$$R_{\chi}=D^c B^{\delta-1}\Gamma^{+} \tag{19}$$

using their estimated values $R_{\xi}^{+}=0.27$, $R_C=0.066$, (i.e. $R=0.66811$), and $R_{\chi}=1.7$ [5].

In practice, we chose xenon as the reference fluid for VLCP. The specific contributions of Z_c and Y_c become evidenced by the $Xe-SF_6$ comparison (where only the contribution of Y_c is significant) and the $Xe-CO_2$ comparison (where both the contributions are mixed). In such conditions, by using all the possible combinations together with experimental values of the three asymptotic amplitudes, Γ^{+}, B and ξ^{+}, we obtained the following empirical values of the constants, ϕ and ζ

$$\phi=1.55\pm 0.15 \tag{20}$$

$$\zeta=-0.12\pm 0.06 \tag{21}$$

The uncertainty of the exponent ζ, because of its small value, reflects two unfavorable conditions for its determination, which are: i) the small differences in the Z_c values for the three selected fluids; ii) the large relative variation of the calculated D^c values resulting from the different choices of the entry pair made of two independent amplitudes.

As of today, there exists a lot amount of experiments for pure fluids close to their critical points to increase the precision on the estimated values of the exponents ϕ and ζ using the method described above. However, our phenomenological approach implies other constraints on ϕ and ζ which permit their determination, specially from scaling arguements. This is because the universality of the sub-class of fluids is necessarily the one predicted by the RG theory. As a particular point, the two only independent critical exponents are ν and δ, selected in section 2 and defined in Table I. Consequently, in conformity with the two hypothesis formulated at the beginning of this section, there are also unequivocal relations between ϕ and ν along the critical isochore and between ζ and δ along the critical isotherm. Here, we immediatly provide the explicit forms of these relations

$$\phi=\frac{1}{\nu},\, with\,\nu=0.63;\,\phi=1.587 \tag{22}$$

$$\phi=\frac{-2}{3\left(\delta+1\right)},\, with\,\delta=4.815;\,\zeta=-0.11465 \tag{23}$$

The above relations will be discussed more in depth in sections 5 and 6 where we introduce the *scale dilatation* of the field distances to the CP on each of these paths which is the only method able to provide the Eqs. (16), (17), (22), and (23). In such a basic approach, we can already pointed out that the *linearization* of the thermal field relation for example (see Eq. (4), added to the

	ξ $(10^{-10}m)$			
	1	2	3	4
Ar	1.5	1.61		
Kr	1.61	1.73		
Xe	1.76	1.89	1.85 ± 0.1	1.86 ± 0.1
CO_2	1.46	1.56	1.5 ± 0.1	1.50 ± 0.1
SF_6	1.84	1.96	1.9 ± 0.1	1.86 ± 0.1
C_2H_6	1.80	1.84	1.8 ± 0.1	
$CClF_3$	1.82		1.95 ± 0.15	
NH_3	1.35	1.44		
C_2H_4	1.73	1.89		
CH_4	1.64	1.72		
N_2	1.54	1.62		
O_2	1.48	1.62		
F_2	1.39			
H_2O	1.20	1.34		
CF_4	1.66			
$p-H_2$	1.63	1.87		
^4He	1.92	2.15		
^3He	2.31	2.67		
C_3H_8	1.89	2.04		

Table II: Values in Å of the asymptotic critical amplitude ξ_0^+ of the correlation length along the critical isochore ($T > T_c$) for neinteen pure fluids.

Column 1 : our determination using equations (9), (11), (16), (22), and (24), with $\xi_0^+ = \alpha_c \xi^+$.

Column 2 : calculated values in a semi-empirical way by Sengers et al (see Ref. [35]).

Column 3 : experimental values obtained by light scattering intensity measurements and turbidity measurements by Garrabos et al in the LIMHP (see Ref. [29]).

Column 4 : experimental values reported by Sengers and Moldover in Ref. [32] and by Sengers in Ref. [33] (for original references of the experimental works see refs. [25, 26, 27, 28]).

recent predictions of Bagnuls and Bervillier [10] for the asymptotic singular power law divergence of the correlation length along the critical isochore, give evidence for the relation $\phi = 1/\nu$.

With the values of ϕ and ζ given by Equations (22) and (23), we obtain the constants Y_G and F_G by using the values of the amplitudes Γ^+ and B for xenon, chosen as one standard critical fluid [31, 32, 33, 34]

$$Y_G = 0.380 \tag{24}$$

$$F_G = 0.526 \tag{25}$$

A first time limited justification of the phenomenological equations is provided in Tables II and III.

In Table II, we compare for about twenty or so fluids, the values of the amplitude $\xi_0^+ = \alpha_c \xi^+$obtained by using equations (9), (11), (16), (22) and (24) with experimental data [29, 32, 33] and with their values calculated using a semi-empirical approach [35].

In Table III, we compare for Xe, SF_6, and CO_2, the values of ξ^+, D^c, B, and Γ^+, determined using our method, with their experimental values.

The results given in these Tables show that our hypotheses, introducing the two critical parameters Z_c and Y_c as being the characteristic numbers for the singular domain of pure fluids, are realistic.

V. MASTER SINGULAR BEHAVIOUR OF THERMODYNAMIC POTENTIALS

We have assumed that the contribution of each characteristic factor can be separated along two distinct lines on the phase surface $f(P, \rho, T) = 0$. As a result, the asymptotic form of at least one among the (non-analytic) thermodynamic properties which are defined on each line is also entirely characterized by the factor it is associated with. In all generality, this thermodynamic property comes from the singular contribution of the appropriate thermodynamic potential and acts such as an equation of state. This is why we reformulate our two hypothesis in consideration of the critical behaviour of two thermodynamic potentials, the selection of which were already justified by analogy between pure fluids and magnetic systems of spins [21].

Hypothesis 1: *When scaled by the factor Y_c, the asymptotic behavior of Δp^* - the difference of the dimensionless thermodynamic potential $\left(\frac{p}{T}\right)^*$ from its critical value $\left(\frac{p}{T}\right)^*_c$ at CP - along the critical isochore, in the single phase region, is the same for all pure fluids.*

Hypothesis 2: *When scaled by the factor Z_c, the asymptotic behavior of $\Delta\mu^*_{\bar{p}}$ - the difference of the dimensionless chemical potential $\mu^*_{\bar{p}}$ and its critical value $\mu^*_{\bar{p},c}$ at CP - along the critical isotherm, is the same for all pure fluids.*

In order to view the results predicted from hypothesis 1 and 2, we consider the critical behavior, schematized on one appropriate field-potential diagram, of two different pure fluids, that are labelled by the subscript i, which means $i = I$ and $i = II$. Crossing CP along the thermodynamic path (L), with $\{(L) \equiv \pm$ for the critical isochore, $(L) \equiv c$ for the critical isotherm$\}$, the thermodynamic potential G, with $\{G = \frac{p}{T}, \mu_{\bar{p}}\}$, is a function of the field g, with $\{g = T, n\}$. Figure 1a illustrates the distinction on the two curves $G_i(g) \mid_{(L)}$ with $\{i = I, II\}$. At each critical point $g = g_c$, the potential has the value $G = G_c$. Of particular interest is the potential difference $\Delta G = G - G_c$, which is a function of the field distance $\Delta g = g - g_c$ measured along (L).

The reduction of the quantities ΔG and Δg can involve appropriate combination of the energy scale factor $(\beta_c)^{-1}$, see Eq. (8), and the length scale factor α_c, see Eq. (9). The results of the dimensionless processing are given in Figure 1b where each curve is represented by the

			Xe	SF_6	CO_2
	$m_{\bar{p}}$	$(10^{-26} kg)$	21.803	24.252	7.308
(0)	p_c	(MPa)	5.84	3.76	7.3753
	ρ_c	$(kg\, m^{-3})$	1110	737	467.8
	T_c	(K)	289.74	318.70	304.14
	$\gamma_c^{'}$	$(MPa\, K^{-1})$	0.119	0.0835	0.170
(1)	$(\beta_c)^{-1} = k_B T_c$	$(10^{-21} J)$	4.0	4.4	4.2
	$\alpha_c = \left(\frac{k_B T_c}{p_c}\right)^{\frac{1}{d}}$	$(10^{-10} m)$	8.815	10.54	8.29
	$Z_c = \frac{p_c m_{\bar{p}}}{\rho_c k_B T_c}$		0.287	0.281	0.274
	$Y_c = \gamma_c^{'} \frac{T_c}{p_c} - 1$		4.9	6.08	6.01
(2)	$\xi^{+} = \left(\frac{Y_G}{Y_c}\right)^{\nu}$		0.1997	0.1745	0.175
	$D^{c} = \left(\frac{F_G}{Z_c}\right)^{-\frac{3(\delta+1)}{2}}$		$5.04\, 10^{-3}$	$4.24\, 10^{-3}$	$3.42\, 10^{-3}$
(3)	$\xi_0^{+} = \alpha_c \xi^{+}$	$(10^{-10} m)$	1.76	1.84	1.45
(4)	$\xi_0^{+}\,(exp)$; Table II; Ref. [33]		1.86 ± 0.10	1.86 ± 0.10	1.50 ± 0.10
	$\xi_0^{+}\,(exp)$; Table II; Ref. [29]		1.85 ± 0.10	1.9 ± 0.1	1.5 ± 0.1
(3)	$D_{LGS}^{c} = (Z_c)^{-(\delta+1)} D^{c}$		7.2	6.8	6.3
(5)	$D_{LGS}^{c}\,(min)$; see Ref. [19]		6.13	5.51	5.92
	$D_{LGS}^{c}\,(max)$; see Ref. [19]		7.53	7.10	6.93
(3)	$B_{LGS} = Z_c \left[\left(\frac{R_\chi}{D^c}\right)\left(\frac{R}{\xi^{+}}\right)^{d}\right]^{\frac{1}{\delta+1}}$		1.455	1.575	1.59
(5)	$B_{LGS}\,(exp)$; see Ref. [25]		1.48	1.56	1.54
	$B_{LGS}\,(exp)$; see Ref. [32]		1.42 ± 0.06	1.62 ± 0.06	1.42 ± 0.05
(3)	$\Gamma_{LGS}^{+} = (Z_c)^2 \left(\frac{R_\chi}{D^c}\right)^{\frac{2}{\delta+1}} \left(\frac{R}{\xi^{+}}\right)^{2-\eta}$		0.0565	0.044	0.046
(5)	$\Gamma_{LGS}^{+}\,(exp)$; see Ref. [32]		0.058 ± 0.002	0.046 ± 0.004	0.046 ± 0.002

Table III: Results for Xe, SF_6, and CO_2 of mass particle $m_{\bar{p}}$.
Lines (0) : Generalized critical parameters of the pure fluids.
Lines (1) : Characteristic parameters of the pure fluids defined by Equations (8) to (11).
Lines (2) : Calculated values of the asymptotic amplitudes ξ^{+} and D^{c} from the characteristics parameters, using Eqs. (8) to (25).
Lines (3) : Calculated values of the asymptotics amplitudes $\xi_0^{+} = \alpha_c \xi^{+}$, D_{LGS}^{c}, B_{LGS}, and Γ_{LGS}^{+} (see Refs. [20, 30, 34]). See the Table I and the text for definitions and estimated values of the amplitude combinations R and R_χ.
Lines (4) : Experimental values of ξ_0^{+} following Table II.
Lines (5) : Values of D_{LGS}^{c}, B_{LGS}, and Γ_{LGS}^{+} obtained by different analyses of the data from the the Fraunhofer diffraction experiments (see Ref. [25]).

following functional form

$$\Delta G^{*} = f_i^{*}\left(\Delta g^{*}\right)\big|_{(L)} \tag{26}$$

Following hypothesis 1 and 2, we can now transform these curves into a master curve, the functional equation of which is given by

$$\mathcal{G}_{\Pi}^{*}\left(\Delta G^{*}\right) = \mathcal{F}_{(L)}^{*}\left[\mathcal{D}_{\Pi}^{*}\left(\Delta g^{*}\right)\right] \tag{27}$$

where $\mathcal{F}_{(L)}^{*}$is a function which does not depend on the pure fluid under consideration but only on the thermodynamic path to cross CP. On the other hand, the new dimensionless functions $\mathcal{G}_{\Pi}^{*}\left(\Delta G^{*}\right)$ and $\mathcal{D}_{\Pi}^{*}\left(\Delta g^{*}\right)$ which appear on equation (27), depend on ΔG^{*} and Δg^{*} through the dimensionless number Π which is characteristic of (L), with $\Pi = Y_c$ for the critical isochore $(L) \equiv \pm$, and $\Pi = Z_c$ for the critical isotherm $(L) \equiv c$. For explaining this dependency, we resort to the general view of the scale dilatation of the physical field [36], which is characterized here by the scale factor Π. The quantities ΔG and Δg transform with dilatation to the following quantities

$$\mathcal{G}_{\Pi}^{*} = \Pi^{E} \Delta G^{*}\big|_{(L)} \tag{28}$$

$$\mathcal{D}_{\Pi}^{*} = \Pi^{e} \Delta g^{*}\big|_{(L)} \tag{29}$$

where $E_{(L)}$ and $e_{(L)}$ are the same values for all the pure fluids. In such conditions, the master curve along (L) described by equation (27) is given in Figure 1c, where the renormalized variables $\mathcal{G}_{\Pi}^{*}$ and $\mathcal{D}_{\Pi}^{*}$ are obtained by equations (28) and (29).

For a better representation of the scale dilatation defined on each path, we derive now the equations (26) to

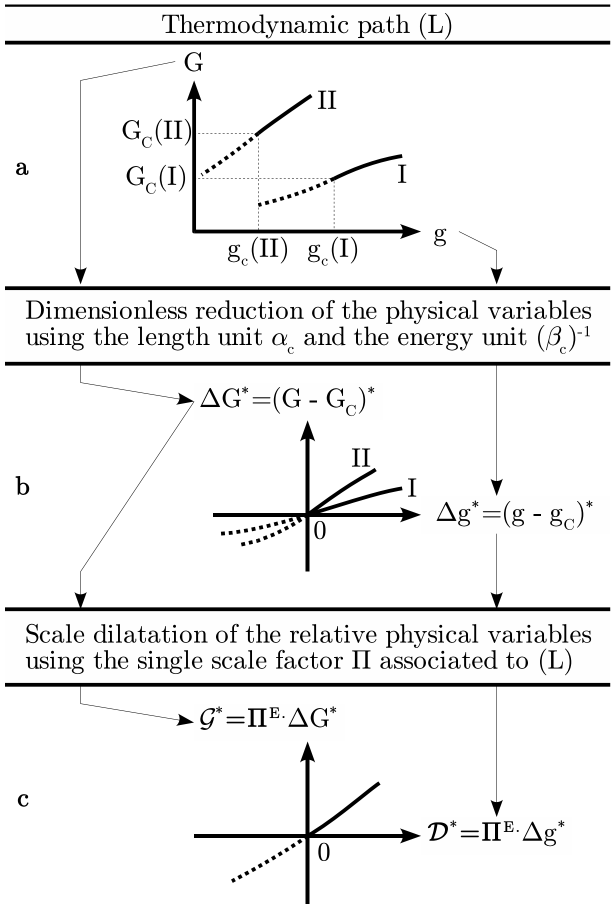

Figure 1: a) Schematic asymptotic behaviours along the critical path (L) of the thermodynamic potential G as a function of the field g, for pure fluids I and II.

b) Schematic asymptotic behaviours of the dimensionless potential difference ΔG^* versus the dimensionless field distance Δg^* to the critical point. The method to make dimensionless the potential G and the field g, involves separately either the length scale factor α_c [see Eq. (9)] or the energy one $(\beta_c)^{-1}$ [see Eq. (8)].

c) Master asymptotic behaviour [see Eq. (27)] along (L) of the renormalized potential $\mathcal{G}^*$ as a function of the renormalized field $\mathcal{D}^*$, for every fluids. This behaviour is obtained using scale dilatations [see Eqs. (28) and (29)] of axes in figure 1b, which take into account the scaling factor Π related to (L). Π is a characteristic parameter of each pure fluid.

(29), and the relations (16) and (17) introduced in the previous section. In these next developments, we will consider only the non-analytic asymptotic contributions of the different functions [12].

A. Scale dilatation along the critical isotherm

The master scaling form of the renormalized chemical potential, $\mathcal{H}^*$ at the critical isotherm is given by [18, 21]

$$\mathcal{H}^* = \mathcal{Z}_H \left|\mathcal{M}^*\right|^{\delta} \tag{30}$$

where $\mathcal{M}^*$ is the renormalised order parameter ($\mathcal{H}^*$ and $\mathcal{M}^*$ are two dual variables with respect to one appropriate renormalized thermodynamic potential). $\mathcal{Z}_H$ is a number which has the same value for all pure fluids. In accordance with equations (28) and (29), we define the following quantities renormalized along the critical isotherm as

$$\mathcal{H}^* = (Z_c)^V \, \Delta\mu^*_{\bar{p}} \tag{31}$$

$$\mathcal{M}^* = (Z_c)^v \, \Delta n^* \tag{32}$$

The asymptotic amplitude, D^c, is related to the reduced physical quantities, $\Delta\mu^*_{\bar{p}}$ and Δn^*, by the following expression

$$\Delta\mu^*_{\bar{p}} = D^c \left|\Delta n^*\right|^{\delta} \tag{33}$$

As a result, we obtain the relation

$$D^c = \mathcal{Z}_H \, (Z_c)^{v\delta - V} \tag{34}$$

which assumes the following form

$$(D^c)^{\frac{1}{V-v\delta}} \, Z_c = (\mathcal{Z}_H)^{\frac{1}{V-v\delta}} \tag{35}$$

equivalent to equation (17).

An examination of equation (35) shows that the values of V and v are linked to δ through equations (17) and (23). The renormalized variables defined by equations (31) and (32) are related by equation (30). Renormalization by only one variable is sufficient to characterize the scale dilatation along the critical isotherm. The two new numbers introduced in this section ($\mathcal{Z}_H$ and one exponent V or v) are linked to F_G and ζ introduced previously through the relation (17). The fact that we have not been able to determine the value of the exponent ζ with certainty in section 4, or the two equivalent exponents V and v in this section, prevents us going further with our phenomenological approach (due to the fact that all the dimensionless quantities can be always defined at an unknown power of Z_c).

B. Scale dilatation along the critical isochore

When approaching CP along the critical isochore in the single phase domain, it is possible to quantify the scale dilatation associated to this path. The reduced differences of physical quantities are expressed in terms of pressure and temperature in the following manners

$$\Delta p^* = \frac{p}{T}\frac{T_c}{p_c} - 1 \tag{36}$$

$$\Delta\tau^* \equiv \tau_S = \frac{T}{T_c} - 1 \qquad (37)$$

In accordance with our hypothesis 1 and the adopted notation, the renormalized variables are defined by the following relations

$$\mathcal{P}^* = (Y_c)^W \Delta p^* \qquad (38)$$

$$\mathcal{T}^* = (Y_c)^w \Delta\tau^* \qquad (39)$$

For $\phi^4_{d=3}(1)$, the non-analytic asymptotic term of the thermodynamic potential $\mathcal{P}^*$ defined along the critical isochore varies as $(\mathcal{T}^*)^{2-\alpha}$ [21, 23]. Particularly for the pure fluid subclass, experiments predominantly show that Δp^* has a term linear in $\Delta\tau^*$, which justifies the addition of one regular contribution, ($\propto \mathcal{T}^*$), to $\mathcal{P}^*$. Considering the dominant regular and non-analytic terms, the master scaling form of the potential $\mathcal{P}^*$ should be given by

$$\mathcal{P}^* = a_1\mathcal{T}^* + \mathcal{Z}^+_P (\mathcal{T}^*)^{2-\alpha} + ... \qquad (40)$$

where a_1 and $\mathcal{Z}^+_P$ take the same values for all pure fluids. Taking into account the definition of the characteristic parameter Y_c, the selection of values $W = 0$ and $w = 1$ for equations (38) and (39) implies that $a_1 = 1$. Accordingly, the renormalized variables are properly defined by the following equations

$$\mathcal{P}^* \equiv \Delta p^* \qquad (41)$$

$$\mathcal{T}^* = Y_c \Delta\tau^* \qquad (42)$$

where Y_c plays the role of the multiplicative factor for the dimensionless thermal distance generally used in experiments.

With these particular choices, the form of equation (17) described in the previous section is now exact. In fact, the singular behavior of the renormalized heat capacity $\mathcal{C}^*$ is proportional to the second derivative of the potential considered above. Correspondingly, the asymptotic amplitude A^+ of the dimensionless singular part Δc^*_V of the physical heat capacity at constant volume, is defined as follows

$$\Delta c^*_V = \frac{A^+}{\alpha} (\Delta\tau^*)^{-\alpha} [1 + ...] \qquad (43)$$

As a result, there is a relation between A^+ and Y_c given by

$$A^+ = \mathcal{Z}^+_A (Y_c)^{2-\alpha} \qquad (44)$$

where $\mathcal{Z}^+_A$ is a unique value for every pure fluid ($\mathcal{Z}^+_A$ depends on the unique value $\mathcal{Z}^+_P$ and the universal value of α, due to the appropriate definition of the renormalized heat capacity).

As the RG theory predicts the existence of the universal ratio, R^+_ξ (Table 1), we can deduce the following relation from equation (44)

$$(\xi)^{\frac{d}{2-\alpha}} Y_c = (R_\xi)^{\frac{d}{2-\alpha}} \left(\mathcal{Z}^+_A\right)^{\frac{1}{2-\alpha}} \qquad (45)$$

Equation (45) is equivalent (from a constant power exponent) to equation (16) and is to do with the scaling law of Josephon between the critical exponents α and ν (Table I).

The formulation and the steps folllowed in this section for derivation of equation (16) and (17) characterize the non-universal transformations of physical fields. We anticipate that with these transformations, singular behavior of the properties of pure fluids on each of the thermodynamic paths considered here will be identical. These phenomenological results are therefore comparable to the predictions of Bagnuls and Bervillier.

VI. COMPARISON WITH THE THEORETICAL RESULTS OBTAINED BY BAGNULS AND BERVILLIER [10]

Along the critical isochore of pure fluids, we propose the scale dilatation with a phenomenological definition

$$\mathcal{T}^* = Y_c \tau^*_S \qquad (46)$$

which is formally equivalent to the one needed to applied RG thechniques

$$t^* = \vartheta \tau^*_S \qquad (47)$$

Following the work of Bagnuls and Bervillier, the singular behavior of the reduced correlation length depends uniquely on the scaled variable t^*. The asymptotic term of this behavior is given by

$$\ell^*(t^*) = \mathbb{Z}^+_\xi (t^*)^{-\nu} [1 + \mathcal{O}(t^*)] \qquad (48)$$

where $\mathbb{Z}^+_\xi$ is a "universal" constant. Using equations (2) and (48) and taking into account that t^* is given by equation (4), the following relation can be derived

$$\xi^+ = \mathbb{Z}^+_\xi \vartheta^{-\nu} \qquad (49)$$

Equation (49) is comparable to our phenomenological equation (16) which has the form given by

$$\xi^+ = \mathcal{Z}^+_\xi (Y_c)^{-\frac{1}{\phi}} \qquad (50)$$

where the relation $\phi = 1/v$ is evident between the exponents. On the other hand, the value of the phenomenological constant given by

$$\mathcal{Z}^+_\xi = (Y_G)^\nu \qquad (51)$$

equals $\mathcal{Z}_{\xi}^{+} = 0.54$, as calculated from the Y_G value given by equation (24), and is different from the theoretical value of $\mathbb{Z}_{\xi}^{+} = 0.48$, provided by the numerical treatment of $\phi_{d=3}^{4}\,(1)$. This difference is essentially due to the non-universality of the reduction process of the physical quantities. As a matter of fact, equation (48) contains the non-universality of the model, the origin of which is not easy to explain. Nevertheless, it is easy to conceive that both non-universality and the basic hypothesis of RG theory are partly taken into account in the dimensionless reduction of the physical variables. This point is emphasized by Bagnuls and Bervillier [10] and discussed for the case where the fluid is xenon [17].

In equation (50), we separated the non-universality of the pure fluid into two terms which are: i) The dimensionless compression factor, Z_c which is associated with the two chosen units for expressing the variables in reduced form ; ii) The non-universal number Y_c which is the scale factor along the critical isochore. Our approach assumes therefore that $\mathcal{Z}_{\xi}^{+}$ keeps the same numerical value for all pure fluids. Due to a lack of a comparison between the results from the model and the ones from the fluids (specially on the dimensional length scale proper to the model), there is no evident reason for $\mathcal{Z}_{\xi}^{+}$ to be a universal number proper to $\phi_{d=3}^{4}\,(1)$, and therefore equal to the $\mathbb{Z}_{\xi}^{+}$ value found in Ref. [10].

VII. CONCLUSIONS

We assumed that the asymptotic singular behavior of a pure fluid at equilibrium close the gas-liquid critical point can be entirely characterized by four macroscopic parameters. These parameters describe the location of the critical point on the characteristic surface and the tangent plane to this surface at this point. Two of these parameters, $(\beta_c)^{-1} = k_B T_c$ and $\alpha_c = \left(\frac{k_B T_c}{p_c}\right)^{\frac{1}{d}}$, are parameters which are evaluated at CP and have units of energy and length, respectively. The remaining two parameters are $Y_c = \gamma_c' \frac{T_c}{p_c} - 1$ and $Z_c = \frac{P_c m_{\bar{p}}}{\rho_c k_B T_c}$, both of which are dimensionless numbers.

In accordance with the two-scale factor universality predicted by the RG theory, we proposed two relations between the two asymptotic amplitudes ξ^{+} and D^{c} and the parameters, Y_c and Z_c. We thus define a new system dependent set made of 12 theoretical asymptotic amplitudes for $\phi_{d=3}^{4}\,(1)$ and two experimentally accessible parameters, Y_c and Z_c. As a consequence, the critical singular behavior of each pure fluid which is defined in RG approach by the selection of two amplitudes is defined in our phenomenological approach by the four parameters, β_c, α_c, Y_c and Z_c.

We moved forward with two hypothesis for definition of the the singular behavior of the thermodynamic potential along the critical isochore and the critical isotherm. As part of these hypothesis, we proposed a scale factor transformation of the reduced physical fields as functions of the distance to the critical point along these paths. We obtained simple relationships between the two asymptotic amplitudes taken as the system dependent parameters in the RG theory and the characteristic experimental parameters, Y_c and Z_c. Comparison with the results of the GR approach shows that the proposed method of scale factor transformation of physical fields is equivalent to the one in the theoretical approach.

We are now working on testing the universality associated with the contribution of the first term of the non-analytic correction to the asymptotic behavior [10].

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Note added 15 December 2005

To conform with the usual notation of the dimensionless energy such as βE with $\beta = \frac{1}{k_B T}$, the present definition of the energy scale factor corresponds to the inverse of the energy scale factor defined in the initial french version of this paper. In addition, the present length scale notation $\alpha_c = \frac{k_B T_c}{p_c}$ replaces the initial one $a = \frac{k_B T_c}{p_c}$ (to avoid confuse situation with the Helmholtz free energy density $a\,(T,n) = \frac{A(T,V,N)}{V}$). The chemical potential per particle $\mu_{\bar{p}}$ is here labellized with the decorated subcript $\bar{p}$, to make explicit distinctions with the chemical potential per mass unit, noted μ_{ρ}, and with the pressure, noted p. The dimensionless leading amplitudes of the susceptibility, noted C^{+}, C^{-} and C^{c} in the initial french version, are presently noted Γ^{+}, Γ^{-} and Γ^{c} (respectively), to conform with actual standard notations of fluid singularities. In the Table I, a printing power index mistake was corrected in the definition of the universal combination $Q_{\Gamma^{+}}$ which now reads $Q_{\Gamma^{+}} = (\Gamma^{+})^{\frac{\delta+1}{\delta}} \left[(A^{+})^{\delta-1}(D^{c})^{2}\right]^{\frac{1}{\delta}}$. Some font modifications between english and french versions are consistent with actual fonts used in recent related papers.

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