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Scaling behaviour of the fluid subclass near the liquid-gas critical point

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Résumé. — Nous proposons des transformations d'échelle non universelles pour les deux variables physiques mesurant les distances au point critique liquide-vapeur d'un fluide pur le long de son isochore critique et de son isotherme critique. Après avoir effectué ces transformations d'échelle, nous observons des comportements singuliers uniques pour tous les fluides purs proches de leur point critique liquide-vapeur.

Abstract. — Non-universal scale transformations are proposed for the two relevant physical distances to the liquid-gas critical point along the critical isochore and critical isotherm. These scale transformations allow us to observe an identical singular behaviour for all pure fluids near their liquid-gas critical point.

1. Introduction.

In a previous article [1], a phenomenological method was developed to determine the asymptotic singular behaviour for a pure fluid at equilibrium near its liquid-gas critical point. The following introduction gives a brief account of the main assumptions and results of the method before defining the singular scaling behaviour for the pure fluid subclass.

The basic input data are the four critical parameters P_c , T_c , ρ_c , and γ'_c . P_c , T_c and ρ_c are, respectively, the critical pressure, temperature and density. γ'_c is the limiting slope at the liquid-gas critical point common to the pressure along the critical isochore above the critical temperature and to the vapour-pressure curve below the critical temperature. These parameters define the location of the liquid-gas critical point in the P , ρ , T diagram and of the tangent plane to the characteristic surface $f(P, \rho, T) = 0$ at this point.

The basic input data are transformed into four typical quantities as follows

$$\beta_c = k_B T_c \quad (1)$$

$$a = (k_B T_c / P_c)^{1/3} \quad (2)$$

$$Y_c = (\gamma'_c T_c / P_c) - 1 \quad (3)$$

$$Z_c = P_c m / (\rho_c k_B T_c) \quad (4)$$

m is the molecular mass of the constitutive particle.
 k_B is the Boltzmann constant.

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functions of a known mass of a pure fluid are made dimensionless by expressing them in units of an appropriate combination of β_c and a (Eqs. (1) and (2)). β_c and a are respectively an energy and a length defined at the liquid-gas critical point.

As examples of interest for the notation used in the present study the order parameter, the ordering field and the singular potential of the liquid-gas transition are considered. The order parameter is related to the density distance to the critical density while the ordering field is related to the distance to the chemical potential on the critical isochore [2]. With our system of units, the dimensionless order parameter is given by

$$\Delta m = (\rho - \rho_c) a^3 / m. \quad (5)$$

The dimensionless ordering field along the critical isotherm reads

$$\Delta h = (\mu - \mu_c) m / \beta_c \quad (6)$$

where the chemical potential per particle μ is the conjugate variable to the number density ρ/m . μ_c is the chemical potential per particle at the liquid-gas critical point.

The dimensionless potential along the critical isochore is given by [2]

$$\Delta \mathcal{F} = [(P/k_B T) a^3 - 1]_{\rho=\rho_c} = \Delta \mathcal{F}(\tau) \quad (7)$$

where

$$\tau = (T - T_c) / T_c \quad (8)$$

is the dimensionless relevant field related to the temperature distance to the critical temperature along the critical isochore

Y_c is the slope at the liquid-gas critical point of the dimensionless potential given by equation (7). Z_c is the compressibility factor at the liquid-gas critical point.

Because of the way in which we use Y_c and Z_c , we recall briefly the two basic ideas of the phenomenological method developed in reference [1].

We first obtain relations

$$X_i^{(L)} = X_i^{(L)}(Y_c, Z_c), \quad i = (1, \dots, 12) \quad (9)$$

where $X_i^{(L)}$ is the i -th non-universal leading amplitude among the twelve amplitudes of the divergent properties of a given pure fluid in the approach to its liquid-gas critical point along the thermodynamic path (L) [2, 3].

Ten among the twelve equations (9) are predicted by the renormalization group theory (RG), [3] in the form of ten universal ratios between the twelve amplitudes $X_i^{(L)}$. This prediction verifies the two-scale factor universality hypothesis for the (d, n) universality class [4] (d and n are respectively the dimension of space and order parameter). For the fluid subclass belonging to the $(d = 3, n = 1)$ universality class, universal ratios [5] may be rearranged [1] to read

$$X_j^{(L)} = X_j^{(L)}(\xi^+, D^c), \quad j = (1, \dots, 10) \quad (10)$$

where $X_j^{(L)}$ is one of the ten amplitudes related to ξ^+ and D^c selected as independent quantities. ξ^+ is the amplitude of the correlation length divergence along the critical isochore in the one-phase region. D^c is the asymptotic shape amplitude of the critical isotherm for the field conjugate to the order parameter. Taking into account equations (10), two among equations (9) are undetermined. In reference [1], we have assumed that these two equations relate separately ξ^+ and D^c to the characteristic parameters Y_c and Z_c as follows [1]

$$(\xi^+)^{1/\nu} Y_c = Y_G \quad (11)$$

$$(D^c)^{-2/[3(\delta+1)]} Z_c = F_G \quad (12)$$

$\nu = 0.63$ and $\delta = 4.815$ are two universal critical exponents [6] associated with ξ^+ and D^c respectively. Hence, Y_G and F_G are two phenomenological constants with the same numerical values for all pure fluids, so that [1]

$$Y_G = 0.38 \quad (13)$$

$$F_G = 0.526. \quad (14)$$

As a next step, the method presented in reference [1] defines Y_c and Z_c as non-universal scale factors for the measure of the physical distance to the liquid-gas critical point of any pure fluid along its critical isochore and critical isotherm respectively.

The basic idea of (RG) is to assume analytical

relations between the relevant renormalized fields t^* and h^* for the 3-dimensional ϕ^4 model, and the corresponding physical fields of the system (S) [7]. We develop an approach analogous to the theoretical one. We allow analytical relations between the relevant rescaled fields $\Delta\mathcal{T}^*$ and $\Delta\mathcal{H}^*$ for the fluid subclass scaling behaviour, and the reduced physical fields τ and Δh for each member of this subclass. These scale transformations read as follows

$$\Delta\mathcal{T}^* = (Y_c)^\gamma \tau \quad (15)$$

$$\Delta\mathcal{H}^* = (Z_c)^z \Delta h \quad (16)$$

where τ and Δh are respectively defined by equations (8) and (6). We postulate that the exponents γ and z have the same numerical values for all pure fluids.

In reference [1], we only gave the explicit scale transformation along the critical isochore. When the rescaled thermodynamic potential $\Delta\mathcal{F}^*$ along the critical isochore above the critical temperature is identified with $\Delta\mathcal{F}$ defined by equation (7), we find again the form of equation (11) using the numerical value $\gamma = 1$ for the exponent γ in equation (15).

The main purpose of the present work is to complete these scale transformations by the phenomenological assignment of the numerical value $z = -3/2$ to the exponent z .

In section 2 we determine leading contributions to the fluid subclass scaling behaviour. They are entirely defined by our choice for numerical values of the exponents γ and z and the constants Y_G and F_G .

In section 3, we present the scaling behaviour of the rescaled isothermal susceptibility along the critical isochore above the critical temperature using experimental results for several pure fluids. Some interesting qualitative features are observed beyond the range of validity of the asymptotic scaling behaviour.

In the same way, section 4 deals with rescaled form of the top of the liquid-gas coexistence curve below the critical temperature.

We conclude that the fluid subclass scaling behaviour can be governed by the same non-universal Y_c and Z_c scale factors at least up to the first order of the non-analytical corrections in the Wegner expansion [8, 9].

2. Leading contributions to the scaling behaviour.

To formulate the scaling behaviour of the rescaled singular property $\mathcal{X}^*$ we assume that

$$\mathcal{X}^* = \mathcal{F}_{(L)}^*(\Delta x^*) \quad (17)$$

where $\mathcal{F}_{(L)}^*$ is a function which only depends on the scaling distance Δx^* to the liquid-gas critical point along the thermodynamic path (L).

The analogy between our phenomenological approach and the (RG) fundamental one requires an asymptotic scaling behaviour which is entirely charac-

terized by the two scale transformations proposed in the introduction

$$\Delta \mathcal{G}^* = Y_c \tau \quad (18)$$

$$\Delta \mathcal{H}^* = Z_c^{-3/2} \Delta h. \quad (19)$$

Equations (18) and (19) define the scaling distances Δx^* along the critical isochore and critical isotherm respectively. Thus, leading amplitudes of the non-analytical contribution to equations (17) are inferred from equations (11) to (14).

For instance, we consider the asymptotic shape for the critical isotherm given by the scaling form

$$\Delta \mathcal{H}^* = \tilde{\mathcal{Z}}_D^c |\Delta \mathcal{M}^*|^\delta \quad (20)$$

where $\tilde{\mathcal{Z}}_D^c$ is assumed to have the same numerical value for all pure fluids. $\Delta \mathcal{M}^*$ is the rescaled order parameter related to the dimensionless one by

$$\Delta \mathcal{M}^* = Z_c^{3/2} \Delta m. \quad (21)$$

Now, we recall that the following asymptotic shape of the critical isotherm

$$\Delta h = D^c |\Delta m|^\delta \quad (22)$$

is assigned to each pure fluid [2]. When equations (19) and (21) are substituted into equation (20) and the result compared with equation (22), we obtain again equation (12). The relationship between the leading amplitude $\tilde{\mathcal{Z}}_D^c$ and the phenomenological constant F_G , (Eq. (14)), is given by

$$\tilde{\mathcal{Z}}_D^c = (F_G)^{-3(\delta+1)/2}. \quad (23)$$

Applying the same reasoning to the scaling behaviour of the correlation length along the critical isochore above the critical temperature we find

$$\tilde{\mathcal{Z}}_\xi^+ = (Y_G)^\nu \quad (24)$$

where $\tilde{\mathcal{Z}}_\xi^+$ is the corresponding leading amplitude. $\tilde{\mathcal{Z}}_\xi^+$ and $\tilde{\mathcal{Z}}_D^c$ are the basic independent variables for the twelve amplitudes of the fluid subclass scaling behaviour as ξ^+ and D^c are the basic ones for the twelve amplitudes of the non-universal behaviour of each member of this subclass. Consequently, the amplitude $\tilde{\mathcal{Z}}_{Xj}^{(L)}$ for any leading contribution to the function $\mathcal{F}_{(L)}^*$ on equation (17) is obtained by the universal form

$$\tilde{\mathcal{Z}}_{Xj}^{(L)} = \tilde{\mathcal{Z}}_{Xj}^{(L)} (\tilde{\mathcal{Z}}_\xi^+, \tilde{\mathcal{Z}}_D^c) \quad (25)$$

while the universal equation (10) allows to calculate $X_j^{(L)}$ from ξ^+ and D^c .

According to the assessment of the status of the fluid critical behaviour made by Levelt Sengers and Sengers [2], Sengers [10] and Moldover [11], the isothermal compressibility and the shape of the top of the coexistence curve are properties for which experimental thermodynamic data in a more conven-

tional range and experimental optical data sufficiently close to the liquid-gas critical point are available for several fluids [2, 10-12]. In the next sections, a comparison is made using these data to test the validity of our phenomenological conjecture presented here.

3. Scaling behaviour of the isothermal susceptibility.

In agreement with phenomenological equation (17), the asymptotic scaling behaviour of the rescaled isothermal susceptibility $\mathcal{S}_T^*$ on the critical isochore above the critical temperature will be given by the scaling form

$$\mathcal{S}_T^*(\Delta \mathcal{G}^*) = \tilde{\mathcal{Z}}_C^+ (\Delta \mathcal{G}^*)^{-\gamma} \quad (26)$$

where $\gamma = 1.24$ is the universal critical exponent [6]. The numerical value of the leading amplitude $\tilde{\mathcal{Z}}_C^+$ is determined by equation (25), so that

$$\tilde{\mathcal{Z}}_C^+ = (R_\chi / \tilde{\mathcal{Z}}_D^c)^{2/(\delta+1)} (\tilde{\mathcal{Z}}_\xi^+ / R)^{(\delta-1)/[d(\delta+1)]} \quad (27)$$

where $R_\chi = 1.7$, $R = R_\xi^+ (R_c)^{-1/d}$, (with $R_\xi^+ = 0.27$ and $R_c = 0.066$, $R = 0.668$) are theoretical universal ratios [5]. Using results obtained by equations (24), (23), (13) and (14), we find

$$\tilde{\mathcal{Z}}_C^+ = 0.12. \quad (28)$$

The relationship between the rescaled isothermal susceptibility, $\mathcal{S}_T^* = [\partial(\Delta \mathcal{M}^*)/\partial(\Delta \mathcal{H}^*)]_T$, and the dimensionless isothermal susceptibility, $\chi_T = [\partial(\Delta m)/\partial(\Delta h)]_T$, reads

$$\mathcal{S}_T^* = Z_c^3 \chi_T. \quad (29)$$

In equation (29), χ_T follows from the reduction process of the isothermal compressibility, $\kappa_T = \rho^{-1}(\partial \rho / \partial P)_T$, using β_c and a as proper units, so that

$$\chi_T = \rho^2 \kappa_T \beta_c a^3 / m^2. \quad (30)$$

Thus the rescaled isothermal susceptibility on the critical isochore above the critical temperature can be written in a more convenient form as

$$\mathcal{S}_T^* = Z_c \kappa_T^* = Z_c \kappa_T P_c \quad (31)$$

since the isothermal compressibility is usually reduced by the critical pressure ($\kappa_T^* = \kappa_T P_c$) [2].

When the experimental values of the product $Z_c \kappa_T^*$ are plotted as a function of the scaling distance $Y_c \tau$, then the scaling equation (26) predicts that the different curves $\kappa_T^*(\tau)$ for each pure fluid should all collapse onto one single curve.

A plot of these experimental data for several pure fluids is shown in figure 1. Two distinct ranges on $\Delta \mathcal{G}^*$ are apparent depending on whether either the optical or the thermodynamic data are considered [10-12]. A detailed discussion of these experimental ranges is given in references [10] and [11].

Fig. 1. — Scaled isothermal susceptibility data for different pure fluids as a function of the scaling distance $Y_c \tau$ along the critical isochore above the critical temperature (see text). Inset shows fitted results of κ_T^* versus τ for Xe, H_2O and He using the scaled equation of state of Levelt Sengers *et al.* [12]. For references and detailed discussion of original experiments see references [2, 10-12].

The results of interferometric measurements obtained from gradient profiles in Xe, CO_2 and SF_6 show a single scaled behaviour in agreement with the phenomenological asymptote (Eqs. (26) and (28)). With our numerical value assigned to the phenomenological constant $\tilde{\alpha}_C^+$, we recall that the leading amplitude determinations for each of the three pure fluids above are within the error of the results obtained by interferometric measurements (see Table III in

Ref. [1]). The experimental precision in this asymptotic range is about 10 %. Furthermore, these experiments have shown that the fluid critical exponents are approaching those for the theoretical model. Nearest to the liquid-gas critical point, the amplitude agreement is then a convincing test for the asymptotic character of our scaling behaviour.

In figure 1, results of thermodynamic measurements are of special interest in view of the qualitative scaling

behaviour in the range far from the liquid-gas critical point. Applying the previous scale transformations to horizontal and vertical axes respectively, the different plots of $\kappa_T^*(\tau)$ for eleven pure fluids fall on the single dotted line as shown in figure 1. To clarify the effects of scale transformations we have represented in the inset the variation of κ_T^* as a function of τ for Xe, H₂O and He. Xe was selected as a simple fluid, H₂O as a polar fluid and He as a quantum fluid for their significant differences in numerical value of Y_c and Z_c scale factors. Instead of the experimental data it is convenient to use the empirical scaled equation of state of Levelt Sengers *et al.* [12] with the effective value of critical exponents ($\gamma_{\text{effective}} = 1.19$).

Thus, in order to connect our phenomenological single scaled asymptotic behaviour of S_T^* with scaled results inferred from conventional thermodynamic measurements in a wider range, we propose to modify equation (26) in the following way

$$S_T^*(\Delta\mathcal{G}^*) = \tilde{Z}_c^+ (\Delta\mathcal{G}^*)^{-\gamma} [1 + \tilde{\alpha}_c^{(1)} (\Delta\mathcal{G}^*)^4] \quad (32)$$

where we assume that the first confluent amplitude $\tilde{\alpha}_c^{(1)}$ has the same numerical value for all pure fluids. $\Delta = 0.5$ is the theoretical universal exponent [13, 6].

Indeed, as was noted by Sengers [10], past experience has shown the necessity to use Wegner expansion [8] for pure fluids in order to reconcile the optical data

with those obtained in conventional ranges. The qualitative scaled behaviour represented by the dotted curve in figure 1 is an illustration of the effect of Wegner expansion terms which make substantial contribution to the departure from the leading scaling contribution (dash-dotted line on Fig. 1). Unfortunately, the amplitudes of the Wegner correction terms depend in a complicated way on the non-universal constants appearing in the theory [8, 9]. These constants are related to the two relevant scaling fields which vanish at the liquid-gas critical point and to others irrelevant scaling fields approaching a finite value at this same point. In the present status of the theoretical development, the dependence of Wegner amplitudes on the non-universal scale factors of real systems is not known.

Consequently, in view of the two-scale factor universality, the meaning of our phenomenological hypothesis expressed by equation (32) is clear : we assume that only the non-universal scale factors Y_c and Z_c govern the asymptotic scaling behaviour as well as the first correction-to-scaling behaviour of critical fluids. Thus, the ratio $\tilde{\alpha}_c^{(1)}/\tilde{Z}_c^+$ is a characteristic number for the fluid subclass.

A comparison between experimental results of κ_T for six pure fluids and the calculated values from equation (32) with the amplitude $\tilde{\alpha}_c^{(1)} = 0.7$ selected by iteration is presented in figure 2. The range of

Fig. 2. — Plot of the isothermal compressibility deviations as a function of $T - T_c$ for Xe, SF₆, CO₂, C₂H₄, H₂O and He. The base line are calculated from the phenomenological scaled equation (32) for $Y_c \tau \lesssim 0.05$ and by the empirical equation $Z_c \kappa_T P_c = 0.1683 (Y_c \tau)^{-1.16665}$ in the range $0.1 \lesssim Y_c \tau \lesssim 0.5$ (see text). The value of $T - T_c$ for each pure fluid corresponding to $Y_c \tau = 0.1$ is represented by a vertical bar superimposed on the logarithmic scale of the horizontal axis of temperature distances. Full curves 1 to 9, experimental data fitted by non-analytical expansions defined from the numerical values of table I. The dotted curves are asymptotic extrapolations from the full curves when the value of the critical exponent is the RG theoretical one ($\gamma = 1.24$); ○ [15]; ●, $T = T_c + 0.6677$ K : reference temperature of [15] with $\kappa_T = 19.64$ (MPa)⁻¹; □ [20]; △ [26]; ◆, ◆, ◆, reference temperatures of [18] with data listed in table II; ○, □, ▽, △, ×, ◆, temperature distances in the practical range $0.1 \lesssim Y_c \tau \lesssim 0.5$ (see text) with data listed in table III.

applicability of equation (32) is limited to $Y_c \tau \lesssim 0.05$. This equation reproduces the experimental data of Xe [14, 18], SF₆ [14, 18-22], CO₂ [14, 18, 23, 24], C₂H₄ [18, 25-27], H₂O [10, 12, 18, 28] and He [10, 12, 18, 29-31] which are reported in tables I and II.

Curves 1, 2 and 3 show that interferometric measurements of the asymptotic behaviour for Xe, SF₆ and CO₂ are very well represented by equation (32). As previously pointed out, the asymptotic behaviour of these curves confirms that the leading amplitudes scaled with Y_c and Z_c indeed attain the proposed single value of $\tilde{\chi}_c^+$, equation (28), with differences which do not exceed 3 %. Note for these three fluids that the recent light-scattering measurements [15, 19, 23], curves 4, 5 and 6, are in agreement with our phenomenological predictions from equation (32). Thus, the

connection with reference temperatures from critical temperature defined by table II are correctly carried out. These reference temperatures are chosen sufficiently distant to the critical temperature for accurate determination of κ_T from P, ρ, T measurements by a graphical method [18]. Xe, SF₆ and CO₂ data are a careful test of our postulate about the single amplitude value for the first Wegner correction term.

With the addition of the deviation plots in the case of C₂H₄, H₂O and He obtained in the temperature range of thermodynamic data, figure 2 shows clearly that the maximum difference is about the error in the experimental determination of κ_T . For example, curves 9a and 9b in the He case are an illustration of the typical scatter in experimental results for these properties. In the same way, it is interesting to observe

Table I. — Literature results for the fit of the isothermal compressibility data by non-analytical expansions (line 1). The numbers in the first column are those of the corresponding deviation curves represented in figure 2 on the experimental temperature range for each pure fluid (see text).

Fig. 2	Fluid	$\kappa_T^* = \Gamma \tau^{-\gamma} (1 + a_1 \tau^4 + a_2 \tau^{24} + a_3 \tau^{34})$						Ref.
		γ	Γ	Δ	a_1	a_2	a_3	
1	Xe	1.24	0.058	—	—	—	—	[14]
2	SF ₆	1.24	0.046	—	—	—	—	[14]
3	CO ₂	1.24	0.046	—	—	—	—	[14]
4	CO ₂	1.219	0.05716	—	—	—	—	[23]
5	SF ₆	1.241	0.0425	0.5	1.14	— 3.04	—	[19, 15]
6	Xe	1.241	0.0577	0.496	1.29	— 1.55	1.9	[15]
7	C ₂ H ₄	1.24	0.057386	0.5	0.55676	—	—	[25]
8	H ₂ O	1.19	0.0751	—	—	—	—	[10]
9a	He	1.1743	0.1611	—	—	—	—	[29, 12]
9b	He	1.188	0.1589	—	—	—	—	[30, 12]

Table II. — Reference temperatures from the critical temperature where our determinations [18] by a graphical method of the isothermal compressibility data are obtained from accurate P, ρ, T measurements. These data referred by the symbol in the first column have been compared to the values calculated by equation (32), see figure 2 and text.

Fig. 2	Fluid	$T - T_c$ (K)	$(\partial P / \partial \rho) \rho_c$ (bar/g/cm ³)	κ_T (MPa) ⁻¹	Ref.
⊙	Xe	1	—	12.1	[16]
■	SF ₆	4.45	4.66 ± 0.10	2.92	[21]
▲	CO ₂	1.054	2.6 ± 0.07	8.2	[24]
		3.721	12.0 ± 0.1	1.78	
▼	C ₂ H ₄	1.8	—	6.3	[26]
✱	H ₂ O	0.58	2.25 ± 0.10	1.38	[28]
		1.11	4.85	6.4	
		1.17	5.2 ± 0.2	5.96	
◆	He	0.071	1.35 ± 0.07	10.65	[31]
		0.128	2.65 ± 0.07	5.42	
		(0.072)	(1.42)		[30]
		(0.123)	(2.55)		

Table III. — *Temperature distances to the critical temperature in the range defined by $0.1 \lesssim Y_c \tau \lesssim 0.5$ (see text). The experimental isothermal compressibility data referred by the symbol in the first column have been compared to the calculated values obtained from the practical relation $Z_c P_c \kappa_T = 0.1683 (Y_c \tau)^{-1.16665}$, see figure 2.*

Fig. 2	Fluid	$T - T_c$	$(\partial P / \partial \rho)(T - T_c, \rho_c)$	$\kappa_T(T - T_c, \rho_c)$	Ref.
⊙	Xe	8.41 K	9.6 bar/g/cm ³		[17]
		13.41 K	16.4		
		23.41 K	30.7		
		33.41 K	46.2		
▽	CO ₂	9.08 K	35.0 bar/g/cm ³		[24]
		18.7 K	8.2		
□	SF ₆	14.478 K	0.126386 bar/Amagat		[21, 22]
△	C ₂ H ₄	10.8 K		0.0736 bar ⁻¹	[26, 27]
		15.8 K		0.0473 bar ⁻¹	
×	H ₂ O	26.159 K	20.4 bar/g/cm ³		[28]
◇	He	0.184 K	4.2 bar/g/cm ³		[31]
		0.298 K	7.3		
		0.409 K	10.5		
		0.686 K	19.5		
		0.96 K	28.5		

the plots presented for C₂H₄ where our equation (32) is a better representation than the fundamental equation proposed by Levelt Sengers *et al.* [25] for the results of accurate Douslin and Harrison measurements.

Moreover the validity of the single scaled behaviour seems to have a more extended range than those of validity of equation (32). A comparison between experimental results of table III and the calculated values from the empirical equation

$$Z_c \kappa_T^* = 0.1683 (Y_c \tau)^{-1.16665}$$

in the range $0.1 \lesssim Y_c \tau \lesssim 0.5$ is also presented in figure 2. The plot reveal a good agreement interesting for practical purposes or if a Wegner expansion with sufficient number of terms is used for the representation of the single scaled behaviour beyond the value $Y_c \tau = 0.05$.

The choice of the six pure fluids is significant for their differences in the non-universal scale factors. Moreover, four decades in $T - T_c$ are covered in figure 2 by the plot of deviations of isothermal compressibility data. Thus we conclude that the scale transformations are acceptable in order to observe the single scaled behaviour for all pure fluids with equation (32) as a good approximation to this single behaviour in the range $Y_c \tau \lesssim 0.05$.

4. Scaling behaviour of the coexistence curve.

In order to describe the two-phase region of pure fluids it is convenient to substitute the following new variable

instead of the rescaled order parameter defined by equation (21)

$$\Delta \mathcal{M}_{LV}^* = Z_c^{3/2} \Delta m_{LV} \quad (33)$$

where the dimensionless difference Δm_{LV} is given by

$$\Delta m_{LV} = (\rho_L - \rho_V) a^3 / 2 m. \quad (34)$$

ρ_L and ρ_V are the liquid and vapour densities. In addition, we define the practical difference

$$\Delta \rho^\pm = (\rho_L - \rho_V) / 2 \rho_c \quad (35)$$

where densities are reduced by ρ_c . Using equations (34) and (35) the rescaled variable $\Delta \mathcal{M}_{LV}^*$ is obtained as

$$\Delta \mathcal{M}_{LV}^* = Z_c^{1/2} \Delta \rho^\pm. \quad (36)$$

On the basis of equation (17), the asymptotic equation for the liquid-gas coexistence curve is

$$\Delta \mathcal{M}_{LV}^*(\Delta \mathcal{T}^*) = \tilde{\mathcal{Z}}_B |\Delta \mathcal{T}^*|^\beta \quad (37)$$

where $\beta = 0.325$ is the universal critical exponent [6]. The numerical value of the leading amplitude $\tilde{\mathcal{Z}}_B$ is determined from the following relation

$$\tilde{\mathcal{Z}}_B = [(R_c / \tilde{\mathcal{Z}}_D^c) (R / \tilde{\mathcal{Z}}_c^+)^d]^{1/(\delta+1)} \quad (38)$$

where the two ratios in the bracket were defined in equation (27). We find

$$\tilde{\mathcal{Z}}_B = 0.465. \quad (39)$$

In figure 3, we show that the scaling plots of $Z_c^{1/2} \Delta \rho^\pm$ versus $|Y_c \tau|$ obtained from results of

Fig. 3. — Scaled liquid-gas coexistence data for different pure fluids as a function of the scaling distance $|Y_c \tau|$ to the critical point (see text and legend of figure 1 for details).

interferometric measurements in Xe, CO₂ and SF₆, can indeed be projected onto the single asymptotic curve predicted by equations (37) and (39). This result supports our hypothesis for the fluid subclass scaling behaviour. In that case, the phenomenological determination of the leading amplitude is within the experimental precision of 5% (see Table III in Ref. [1]).

When the ranges far from the liquid-gas critical point are investigated, the scaled thermodynamic behaviour of ΔM_{LV}^* shown in figure 3 is similar to the scaled thermodynamic behaviour found for S_T^* (see Fig. 1). In order to make a quantitative illustration of scale transformations in that region we fit again the curves $\Delta\rho^\pm(\tau)$ for Xe, H₂O and He with the effective value of the critical exponent ($\beta_{\text{effective}} = 0.355$) [12]. Likewise, using the same arguments as in the previous section, we propose to modify equation (37) as follows

$$\Delta M_{LV}^*(\Delta T^*) = \tilde{Z}_B |\Delta T^*|^\beta [1 + \tilde{a}_B^{(1)} |\Delta T^*|^4] \quad (40)$$

where the first confluent amplitude $\tilde{a}_B^{(1)}$ has the same numerical value for all pure fluids. The value of $\tilde{a}_B^{(1)}$ is related to $\tilde{a}_C^{(1)}$, by the theoretical universal ratio $\tilde{a}_B^{(1)}/\tilde{a}_C^{(1)}$ [32]. However the coexistence curve data for pure fluids have the resolution to determine $\tilde{a}_B^{(1)}$ rather accurately. This complicated task would require inter-comparison between optical results and density data on an absolute basis. As was noted by Moldover [11], the optical measurements exist in a narrow region close to the critical temperature, see figure 3, where confluent singularities probably make a very small contribution to the measured quantities. Conversely, conventional P, ρ, T measurements have sufficient precision to detect confluent singularities in a

temperature range much further from the critical temperature; at such large distances to the critical point several terms in the Wegner expansion may contribute to the measured quantities. Consequently, an investigation of the coexistence curve data as complete as this made for the behaviour of the κ_T data cannot be included in the present work. Instead we specify more accurately how our phenomenological method work for the leading contribution to the scaling behaviour of the coexistence curve for Xe, SF₆, CO₂ [14] and C₂H₄ [25]. The results presented in table IV are a comparison between the proposed single value of $\tilde{Z}_B$, equation (39), and the values of the product $Z_c^{1/2} Y_c^{-\beta} B$ obtained from the experimental amplitude B scaled with Y_c and Z_c . The deviations in Xe, CO₂ and SF₆ cases are of the order of a few percent precision on the indirect density measurements from interferometric methods. For C₂H₄, data on the difference of coexisting densities are obtained over large temperature ranges further from critical temperature. In view of the difficulties in the interpretation of these thermodynamic results discussed above, the difference of 3% stated in table IV is an acceptable level. Furthermore, we note that the agreement in leading contribution obtained from equation (40) using equation (39) is a first necessary step in order to obtain a direct quantitative determination of $\tilde{a}_B^{(1)}$ from density data. This study is currently in progress in our laboratory.

5. Concluding remarks.

According to the phenomenological approach discussed in a previous work [1] a scaling critical beha-

Table IV. — Comparison between the single value of $\tilde{z}_B$, equation (39), and the corresponding values obtained from the experimental amplitudes B scaled with Y_c and Z_c for Xe, SF₆, CO₂ and C₂H₄.

Ref.	β	B_{exp}	$\tilde{z}_B$	%
This work	0.325		0.465	
Xe [14]	0.329	1.48	0.468	+ 0.68
	0.325	1.42 $\pm$ 0.06	0.452	– 2.78
SF ₆ [14]	0.321	1.56	0.463	– 0.52
	0.325	1.62 $\pm$ 0.06	0.477	+ 2.56
CO ₂ [14]	0.321	1.54	0.454	– 2.45
	0.325	1.59 $\pm$ 0.06	0.465	0
C ₂ H ₄ [25]	0.325	1.5639	0.480	+ 3.19

viour for the fluid subclass is expected. This scaling behaviour is obtained after using non-universal scale transformations applied to the dimensionless physical distance τ and Δh to the liquid-gas critical point along the critical isochore and the critical isotherm of any pure fluid. The analysis of experimental data for three different substances in term of these scale transformations yields a good evaluation of the leading contribution for the renormalized isothermal susceptibility and coexistence curve.

Moving away from the critical point the experimental scaling behaviour for both properties analysed above are consistent with their asymptotic scaling picture within the same accuracy. The description of the fluid critical behaviour in this finite range around the critical point does not need to take into account more complicated proposals. With respects

to Wegner expansion, it follows that the irrelevant scaling fields approaching a finite value at the liquid-gas critical point have a very low contribution compared to the leading contribution due to the two relevant scaling fields $\Delta\mathcal{G}^*$ and $\Delta\mathcal{H}^*$ which vanish at the liquid-gas critical point.

From these observations we propose the same amplitude values for the first confluent term of the correction to scaling behaviour for the fluids subclass. Hence we made the assumption that the fluid-dependent quantities Y_c and Z_c which appear through our phenomenological relationships between scaling fields ($\Delta\mathcal{G}^*$, $\Delta\mathcal{H}^*$) and physical ones (τ , Δh), (Eqs. (18) and (19)), are to the first order the only fluid-dependent quantities in the Wegner expansion.

Finally, we must point out that a recent nonlinear (RG) treatment of the 3-dimensional ϕ^4 model along the critical isochore above the critical temperature [33] gives a description of the lowest non-asymptotic critical behaviour in qualitative agreement with our phenomenological model. According to these theoretical calculations, an analysis of experimental data for xenon [34] shows that the knowledge of only two scales determines all critical behaviour up to and including the first Wegner correction. The quantitative deviations between the particular forms predicted by (RG) and our present scaling forms can be related to the dimensionless reduction process of physical quantities [1, 34].

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