

Master singular behavior for the Sugden factor of one-component fluids near their gas-liquid critical point

Yves Garrabos*, Fabien Palencia, Carole Lecoutre
 ESEME-CNRS, ICMCB-UPR 9048, Université Bordeaux 1,
 87 avenue du Docteur Albert Schweitzer, F-33608 Pessac France.*

Daniel Broseta
 Laboratoire des Fluides Complexes, UMR 5150 - Université de Pau et des Pays de l'Adour, B.P. 1155, 64013 Pau Cedex, France.

Bernard Le Neindre
 LIMHP-CNRS-UPR 1311, Université Paris 13, Avenue Jean Baptiste Clément, F-93430 Villetaneuse France.

Can Erkey
 Department of Chemical Engineering, University of Connecticut, Storrs, CT 06074 USA.
 (Dated: 9 Nov. 2006)

We present the master (i.e. unique) behavior of the squared capillary length - the so-called Sugden factor -, as a function of the temperature-like field along the critical isochore, asymptotically close to the gas-liquid critical point of about twenty (one-component) fluids. This master behavior is obtained using the scale dilatation of the relevant physical fields of the one-component fluids. The scale dilatation method introduces the fluid-dependent scale factors in a manner analog to the linear relations between physical fields and scaling fields needed by the renormalization theory applied to any physical system belonging to the Ising-like universality class. The master behavior for the Sugden factor satisfies hyperscaling. It can be asymptotically fitted by the leading terms of the theoretical crossover functions for the correlation length and the susceptibility in the homogeneous domain, recently obtained from massive renormalization in field theory. In the absence of corresponding estimation of the theoretical crossover functions for the interfacial tension, we define the range of the temperature-like field where the master leading power law can be practically used to predict the singular behavior of the Sugden factor, in conformity with the theoretical description provided by the massive renormalization scheme within the extended asymptotic domain of the one-component fluid "subclass".

PACS numbers: 64.60.-i, 05.70.Jk, 64.70.Fx

1. INTRODUCTION

The knowledge of interfacial properties [1] for a non-homogeneous fluid of coexisting vapor and liquid at equilibrium is of prime importance for many engineering applications and process simulations. Moreover, accurate predictions of these interfacial properties are essential to gain confidence in modeling fluid flow in porous media, oil recovery, gas storage in geological formations, pool boiling phenomena, microfluidic devices based on wetting phenomena, etc.

A large number of different forms of related phenomenological laws, the so-called *ancillary equations*, are reported in the literature to calculate interfacial properties along the vapor-liquid equilibrium (VLE) line [2]. These relations complement the complex multiparameter equations of state (EOS) which have been developed to accurately fit the thermodynamic properties measured in the homogeneous domain. Such a phenomenological approach to estimate fluid properties is commonly based on

the multiparameter corresponding-states principle [2–4]. In the following we call k -CSEOS such an EOS which contains $k \geq 2$ system-dependent parameters. The main reason for the predictive power of such a phenomenological approach is related to the fact that the two-parameter corresponding-states (2-CS) principle can be applied to any polynomial EOS which has a liquid-vapor critical point [5]. However, in spite of increasing the number of fluid-dependent parameters, the common calculation of interfacial properties from ancillary equations and k -CSEOS, is not only mathematically complex, but is also unable to account for:

1) the molecular fluid complexity [3], especially the non-spherical symmetry of molecules and the quantum behavior of light fluids [4];

2) the *asymptotic scaling of the critical phenomena* close to the gas-liquid critical point [6], especially the non-analytic Ising-like nature [7, 8] of the critical exponent [9].

Among these interfacial properties, the capillary length ℓ_{Ca} , or more precisely the squared capillary length $(\ell_{Ca})^2$ also called the Sugden factor [10] and noted S_g in the following, plays a special role on Earth's gravity environment (recalled here by the subscript g). The Sugden

*Electronic address: garrabos@icmcb-bordeaux.cnrs.fr

factor reflects the balance between interfacial and volumic forces, which determines the shape and the position of the interface at equilibrium when subject to the gravity field of constant acceleration g . In the case of perfect liquid wetting, S_g is then related to the surface tension σ and the density difference $\Delta\rho_{LV} = \rho_L - \rho_V$ between coexisting liquid (density ρ_L) and vapor (density ρ_V) phases by the equation

$$S_g = \frac{2\sigma}{g\Delta\rho_{LV}} \quad (1)$$

Therefore, the knowledge of the Sugden factor is an important challenge to provide better control on nonhomogeneous fluid properties.

In addition, as clearly documented two decades ago [11–13], the temperature dependence of S_g , along a large temperature range of the VLE line of all investigated one-component fluids [11, 12, 14–22], shows a pure *power law* behavior which is applicable over an appreciably larger temperature range [see below Eq. (2) and the related discussion of the Fig. 1a]. Such a weak temperature dependence of the effective exponent *at small but finite* distance of the critical point was partly well-understood to be related to the smallest value ($\simeq 0.51$ [9], see below Table III) of the confluent exponents which govern the corrections to asymptotic scaling of critical phenomena [23]. However the theoretical reason to observe a near zero-value of the amplitude contribution of the confluent corrections for the Sugden factor case remains unclear, especially in the absence of estimation of the crossover behavior of the surface tension.

Indeed, the significant theoretical improvements to account for *classical-to-critical crossover* [8], especially in the one-component fluids [6], provide the most powerful tools available today to analyze accurately interfacial properties in large temperature ranges of the non-homogeneous domain. For example in the present work, using the crossover functions recently derived [24, 25] from the massive renormalization scheme in three dimension ($d = 3$) [26–29], our main objective is to accurately estimate this leading asymptotic behavior of S_g from scaling arguments [1, 30–32] and available description [33–35] of the master singular behavior of the one-component fluid “subclass”. Such a description is based on the formal analogy between the scale dilatation of the physical field variables proposed by Garrabos [36–38] and the linear relation between the physical fields and the scaling fields needed by the renormalization theory [39]. The major advantage of this scale dilatation method is to estimate the universal behavior of any one-component fluids *without any adjustable parameter*, by using only the four critical coordinates of its liquid-vapor critical point (excluding here quantum fluids [38] to simplify the presentation of the scale dilatation method).

The paper is organized as follows. Section 2 demonstrates the master singular behavior of S_g observed from the scale dilatation method. The corresponding Ising-like asymptotic description of S_g based on hyperscal-

ing [1, 30–32] and massive renormalization description [26, 28, 29] of the critical crossover is reported in Section 3. The master leading terms of the crossover functions for the correlation length and the susceptibility in the homogeneous domain [24, 25], are used to demonstrate that the master behavior observed in the (nonhomogeneous) extended asymptotic domain can be predicted within the experimental precision. The discussion given in Section 4 shows the main points to be considered for a classical-to-critical crossover description of the interfacial properties at finite temperature distance to the critical temperature. Specifically, we estimate precisely the temperature range where this theoretical treatment becomes inappropriate to represent the increasing non critical microscopic difference between gas and liquid approaching the triple point temperature. Conclusion is given in Section 5.

2. MASTER SINGULAR BEHAVIOR OF THE SUGDEN FACTOR

2.1. The data sources

The Sugden factor measurements $S_g(|\Delta T|)$ as a function of the temperature distance $\Delta T = T - T_c$ to the critical point in the nonhomogeneous range $T < T_c$, have been published and analyzed for several one-component fluids [11–22, 40]. T (T_c) is the temperature (critical temperature). $S_g(|\Delta T|)$ data were generally obtained along the critical isochore $\rho = \rho_c$ in a finite temperature range bounded by max and min values of $|\Delta T| = T_{c,exp} - T$, where $T_{c,exp}$ was the measured (or estimated) critical temperature in the experiments [ρ (ρ_c) is the density (critical density)]. The relative precision claimed by the authors was generally lower than 10%. For most fluids, S_g was fitted using the effective power law [1, 11, 13]

$$S_g = S_{0,e} |\Delta\tau^*|^{\varphi_e} \quad (2)$$

where the dimensionless temperature distance $|\Delta\tau^*|$ to the critical point was defined by

$$|\Delta\tau^*| = \frac{|\Delta T|}{T_{c,exp}} = \frac{T_{c,exp} - T}{T_{c,exp}} \quad (3)$$

In Eq. (2), the free amplitude $S_{0,e}$ was a fluid-dependent quantity related to the effective value $\varphi_e \simeq 0.91 - 0.97$ of the free (or fixed) exponent φ_e considered as a physical parameter when measurements were performed in a restricted temperature range at finite distance to $T_{c,exp}$. The corresponding parameter set $\varphi_e; S_{0,e}$ [with free (or fixed) value of φ_e] for each selected fluid is summarized in columns 3 and 4 of Table I (references are given in column 2 for twenty one-component fluids). However, admitting now that $\Delta\tau^*$ is the relevant physical field [30] to describe the singular scaling behavior of the thermodynamic fluid properties in the homogeneous or nonhomogeneous domains along the critical isochore, the three main *critical phenomena* features of this effective fitting analysis are:

Fluid	Ref	φ_e	$S_{0,e}$ (mm^2)	$S_{0,\varphi}$ (mm^2)	Ref	$\mathcal{Z}_{S,\varphi}$	$\delta\mathcal{Z}_{S,\varphi}$ %
Ar	[17]	0.940	4.13	4.036	[13]	2.423	-1.9
	[12]	0.913	3.78	4.18	This work	2.510	+1.6
Xe	[18]	0.942	3.05	2.953	[13]	2.668	+8.0
N ₂	[17]	0.930	5.46	5.59	This work	2.446	-1.0
	[12]	0.926	5.10	5.32	This work	2.328	-5.7
O ₂	[12]	0.909	4.85	5.47	This work	2.563	+4.6
CO ₂	[19]	0.933	9.47	9.52	[13]	2.55	+3.3
	[12]	0.920	8.40	9.0	This work	2.411	-2.4
SF ₆	[11]	0.943	3.931	3.84	[13]	2.46	-0.4
CCl ₃ F	[11]	0.928	6.234	6.44	This work	2.470	0.0
CCl ₂ F ₂	[11]	0.936	5.615	5.589	This work	2.476	+0.3
CClF ₃	[19]	0.972	5.33	4.5	This work	2.268	-8.1
	[11]	0.9379	4.847	4.783	This work	2.411	-2.4
CBrF ₃	[11]	0.938	3.879	3.826	This work	2.374	-3.1
CHClF ₂	[11]	0.937	6.859	6.796	This work	2.323	-6.0
C ₂ H ₄	[14]			13.90	[13]	2.480	+0.4
CH ₄	[12]	0.933	13.6	13.73	This work	2.382	-3.6
C ₂ H ₆	[14, 16]			14.42	[13]	2.437	-1.3
i - C ₄ H ₁₀	[15]			12.71	[13]	2.392	-3.2
n - C ₅ H ₁₂	[40]	0.935	12.916			2.488	+0.7
n - C ₆ H ₁₄	[40]	0.935	12.753			2.445	-1.0
n - C ₇ H ₁₆	[40]	0.935	12.520			2.552	+3.4
n - C ₈ H ₁₈	[40]	0.935	12.217			2.520	+2.0
H ₂ O	[22]			34.72	[13]	2.262	-8.4
	[21]	0.91	33.2	37.25	This work	2.427	-1.7
$\langle\mathcal{Z}_{S,\varphi}\rangle$						2.4530	± 3.1
\mathcal{Z}_S						2.47	

Table I: Effective exponent φ_e (column 3) and effective leading amplitude $S_{0,e}$ [see Eq. (2)] (column 4) of the Sugden factor $S_g \equiv (\ell_{Ca})^2$ (ℓ_{Ca} is the capillary length) for several one-component fluids (column 1); From data sources and selected fitting results of references given in column 2; Calculated values of the physical amplitude $S_{0,\varphi}$ (column 5) and the master amplitude $\mathcal{Z}_{S,\varphi}$ (column 6); See text for this work and Refs. given in column 5; The residual $\delta\mathcal{Z}_{S,\varphi} = 100 \times \left(\frac{\mathcal{Z}_{S,\varphi}}{\mathcal{Z}_S} - 1 \right)$ (expressed in %) is given in column 7, where the master value $\mathcal{Z}_S = 2.47$ is estimated from Eq. (43).

i) the correlation between the effective values of $S_{0,e}$ and φ_e is highly dependent on $T_{c,exp}$ and on the (min and max) values of the temperature range covered by the fit *close* to the critical point; especially when the local values of φ_e are estimated in the temperature range lower than $|\Delta\tau^*| < 0.05$, the common averaged value $\varphi_e = 0.935 \pm 0.015$, equal to the asymptotic universal value $\varphi = 2\nu - \beta = 0.935 \pm 0.004$ obtained from the present theoretical estimation of the critical exponents $\nu = 0.6304 \pm 0.0013$ and $\beta = 0.3258 \pm 0.0014$ [9] [see below Eq. (5)], appears consistent with the S_g singular behavior, whatever the one-component fluid.

ii) accordingly, the temperature dependence of the effective exponent defined here as $\frac{\partial(\ln[S_g])}{\partial(\ln[|\Delta\tau^*|])}$ over a larger temperature range is very small, whatever the one-component fluid or the extension of the temperature

range of the fit. Therefore the sign of the small amplitude of the leading confluent term cannot unambiguously defined;

iii) the measured value of the effective exponent is never observed to be equal to the mean-field value $\varphi_{MF} = 1$, even in a temperature range far from the critical temperature, whatever the one-component fluid.

As a matter of fact, it is well-established now [8] that the range of validity of the *asymptotic scaling* form of Eq. (2) is *strictly* restricted to the asymptotic approach of the liquid-gas critical point, when $\sigma \propto |\Delta\tau^*|^\phi$ and $\Delta\rho_{LV} \propto |\Delta\tau^*|^\beta$ simultaneously go to zero for $\Delta\tau^* \rightarrow 0$ in Eq. (1). $\phi = (d-1)\nu \approx 1.261$ and $\beta \approx 0.326$ are the universal values [9] of the critical exponents related to the temperature dependence of σ and $\Delta\rho_{LV}$, respectively, and $\nu \approx 0.63$ is the universal value [9] of the critical expo-

nent for the correlation length ξ of density fluctuations, with $\xi \propto |\Delta\tau^*|^{-\nu}$ (see also [8] for details of notations and definitions). However, at small but finite $|\Delta\tau^*|$, any pure power law like Eq. (2) must be modified to account for confluent corrections to scaling which can be represented by the Wegner-like expansion [23] with the universal features of uniaxial 3D Ising like systems [8]. Then, in the case of S_g :

$$S_g = S_0 |\Delta\tau^*|^\varphi \left[1 + \sum_{i=1}^{\infty} S_i |\Delta\tau^*|^{i\Delta} \right] \quad (4)$$

where $\Delta \approx 0.51$ is the universal value [9] of the critical exponent which characterizes the leading family of the confluent corrections to scaling. The amplitudes S_0, S_1, \dots, S_i , etc., are fluid-dependent quantities. Equation (4) means that the effective critical exponent φ_e only takes its universal value

$$\varphi = \phi - \beta = (d-1)\nu - \beta \approx 0.935 \quad (5)$$

asymptotically close to T_c , i.e. when $\Delta\tau^* \rightarrow 0$. Therefore, the weak temperature dependence of the effective exponent at finite value of $\Delta\tau^*$, mainly shows low rate of convergence of the Wegner expansion. Moreover, in the fitting of the experimental S_g data, if the contribution of the confluent correction terms is negligible, then $\sum_{i=1}^{\infty} S_i |\Delta\tau^*|^{i\Delta} \sim 0$ in Eq. (4).

The singular decreasing behavior of the Sugden factor $S_g \equiv (\ell C a)^2 [m^2]$ as a function of the temperature distance $T_c - T [K]$ is illustrated in Fig. 1a [log-log scale] for eighteen one-component fluids. Each curve has a relative temperature extension corresponding to the experimental temperature range (including for some fluids measurements until their triple point temperature T_{TP}). The mean (theoretical) value $\varphi = 0.935$ of the effective slope of these curves is indicated. The S_g values at $T_c - T = 1 K$ cover one decade, from $1.5 \cdot 10^{-8} m^2$ for sulfurhexafluoride [with $S_0(SF_6) = 3.84 mm^2$], to $1.5 \cdot 10^{-7} m^2$ for methane [$S_0(CH_4) = 13.80 mm^2$]. To illustrate the weak temperature dependence of φ_e , the Sugden factor can be divided by $(T_c - T)^\varphi$ (with $\varphi = 0.935$) [13]. Therefore, this convenient scaled form $\frac{S_g}{(T_c - T)^\varphi} [m^2 K^{-\varphi}]$, makes the order of magnitude of the leading amplitude contribution (i.e. $S_g(T = T_c + 1K) \simeq S_0(T_c)^{-\varphi}$) of each fluid clearly distinguishable in Fig. 1b (log-log scale), while the quasi-horizontal line whatever the fluid (except the water case, see § 4.3) shows that the confluent contribution is very small (i.e. $\sum_{i=1}^{\infty} S_i (T_c)^{-i\Delta} (T_c - T)^{i\Delta} \sim 0$).

We have noted that some of the data reported in Fig. 1a have been measured in a large temperature range on the VLE line, including measurements close to T_{TP} . For practical graduation of the temperature axis from the asymptotic critical range to the triple point temperature, we have marked by vertical arrows the temperature

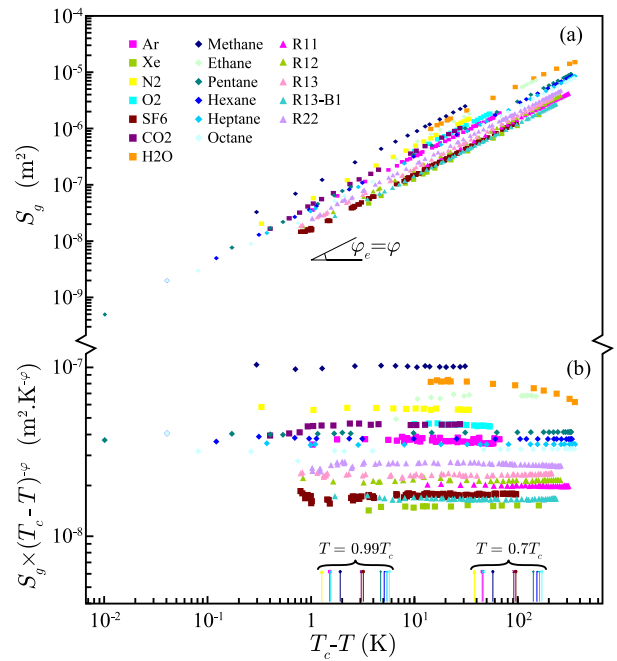


Figure 1: (Color online) a) Singular decreasing behavior (log-log scale) of S_g (expressed in m^2) with effective slope $\varphi_e = 0.935 \pm 0.015 (= \varphi)$, as a function of the temperature distance $T_c - T$, for eighteen nonhomogeneous one-component fluids (see also Tables I and II). Inserted Table gives the color indexation for each fluid. b) Log-Log scale of $\frac{S_g}{(T_c - T)^\varphi}$ (expressed in $m^2 K^{-\varphi}$, with $\varphi = 0.935$), as a function of the temperature distance $T_c - T$, which shows the weak temperature dependence of the effective exponent φ_e . For each fluid, two arrows indicate the practical temperature distances of $T_c - T = 0.01T_c$ and $T_c - T = 0.3T_c$, respectively [see text for detail].

distance where $T = 0.7T_c$ (i.e., the temperature used to define the practical fluid-dependent acentric factor [41]). The temperature range between $0.3T_c \leq T_c - T \leq T_c - T_{TP}$ (the right hand side of the corresponding arrows in Fig. 1a) is considered to be *far away* from the critical point. In the opposite direction when $T_c - T \rightarrow 0$, the practical temperature range where the Wegner-like expansion fits the singular behavior does not usually exceed a few percent in $|\Delta\tau^*|$ [42]. To distinguish the asymptotic temperature range $T_c - T \leq 0.01T_c$ *close* to the critical point where the use of Eq. (4) has a theoretical justification, as discussed below in § 3, vertical arrows at $T = 0.99T_c$ have been added in Fig. 1a). To introduce the main physical parameters needed for accurate description of the singular behavior of S_g in this asymptotic temperature range, the next subsection presents the application of the scale dilatation method [36, 37] leading to define the dimensionless form (noted S_g^*) and the renormalized form (noted S_{g^*}) of the Sugden factor, with two objectives:

1) to show that any modeling based on the 2-CS principle is inaccurate to describe the fluid dependence of

Fluid	$m_{\bar{p}}$ ($10^{-26} kg$)	T_c (K)	$v_{\bar{p},c}$ (nm^3)	p_c (MPa)	γ'_c ($MPa K^{-1}$)	$(\beta_c)^{-1}$ ($10^{-21} J$)	α_c (nm)	Z_c	Y_c
Ar	6.634	150.725	0.12388	4.865	0.191	2.08099	0.753463	0.2896	4.32882
Xe	21.803	289.733	0.19589	5.84	0.1182	4.0003	0.881508	0.28601	4.85434
N ₂	4.652	126.214	0.14814	3.398	0.1715	1.74258	0.80043	0.288875	5.37014
O ₂	5.314	154.580	0.12187	5.043	0.1953	2.13421	0.750786	0.287972	4.98641
CO ₂	7.308	304.137	0.15622	7.3753	0.170	4.19907	0.82882	0.27438	6.0104
SF ₆	24.255	318.735	0.32769	3.754	0.0835	4.40062	1.0544	0.27954	6.0896
CCl ₃ F	22.810	471.110	0.41174	4.4076	0.0655	6.50438	1.13850	0.27901	6.00530
CCl ₂ F ₂	20.078	384.930	0.35562	4.1249	0.0745	5.31454	1.08814	0.27602	5.95186
CClF ₃	17.348	301.88	0.29807	3.877	0.0910	4.16791	1.02441	0.27727	6.08861
CBrF ₃	24.727	340.19	0.33191	3.956	0.0810	4.69683	1.05889	0.27956	5.96985
CHClF ₂	14.359	369.30	0.27454	4.990	0.0965	5.09874	1.00721	0.26869	6.14259
C ₂ H ₄	4.658	282.345	0.21667	5.042	0.11337	3.89820	0.91781	0.28131	5.34856
CH ₄	2.664	190.564	0.16361	4.5992	0.14442	2.63102	0.830133	0.28679	4.9838
C ₂ H ₆	4.993	305.322	0.24171	4.872	0.10304	4.21554	0.95290	0.27935	5.45505
<i>i</i> - C ₄ H ₁₀	9.652	407.844	0.43020	3.629	0.0610	5.63084	1.15770	0.27726	5.93407
<i>n</i> - C ₅ H ₁₂	11.981	469.70	0.521785	3.3665	0.0511	6.48491	1.24425	0.270875	6.12956
<i>n</i> - C ₆ H ₁₄	14.310	507.49	0.61138	3.0181	0.043658*	7.00666	1.3186	0.26667	6.30719
<i>n</i> - C ₇ H ₁₆	16.6386	540.13	0.7168	2.727	0.038068*	7.45731	1.3983	0.26218	6.64356
<i>n</i> - C ₈ H ₁₈	18.9683	568.88	0.81839	2.486	0.033768*	7.85424	1.46746	0.258978	6.82776
H ₂ O	2.991	647.067	0.09268	22.046	0.275	8.93373	0.740	0.229	7.071

Table II: Set of critical parameters [see Eqs. (6) and (7)] for twenty one-component fluids of particle mass $m_{\bar{p}}$ [43].

dimensionless S_g^* [see below Eq. (12)] as a function of the dimensionless temperature field $|\Delta\tau^*| = \frac{T_c - T}{T_c}$;

2) to unambiguously show the master singular behavior of renormalized S_g^* [see below Eq. (18)] as a function of the renormalized temperature-like field, noted \mathcal{T}^* [see below Eq. (14)].

2.2. The scale dilatation method to observe the master singular behavior

The following analysis of the Sugden factor from the scale dilatation method is similar to the one of the correlation length given in Ref. [33]. Therefore, we recall only the main features of the scale dilatation method (ignoring the quantum contributions at $T \cong T_c$ [38]). The input data are the four critical coordinates

$$Q_{c,a_{\bar{p}}}^{\min} = \left\{ T_c, v_{\bar{p},c}, p_c, \gamma'_c = \left[\left(\frac{\partial p}{\partial T} \right)_{v_{\bar{p},c}} \right]_{CP} \right\} \quad (6)$$

which localize the liquid gas critical point on the phase surface of equation of state $\Phi_{a_{\bar{p}}}^p(p, v_{\bar{p}}, T) = 0$, for each fluid particle of mass $m_{\bar{p}}$ [43]. p is the pressure, $v_{\bar{p}}$ is the particle volume, and $a_{\bar{p}}(T, v_{\bar{p}})$ is the Helmholtz energy per particle. The subscript \bar{p} refers to a particle quantity and all the definitions and notations related to Eq. (6) are given in [36–38]. The critical data related to the fluids selected in Table I are reported in Table II. We note

that the T_c values of Table II, which were obtained from the thermodynamic analysis of the phase surface, can be slightly different from the $T_{c,exp}$ values given in the experiments referred in Table I. Also $\rho_c = \frac{m_{\bar{p}}}{v_{\bar{p},c}}$ values from Table II can be slightly different from the experimental critical density values reported in these experiments.

In combining $Q_{c,a_{\bar{p}}}^{\min}$, the Boltzmann constant k_B , and space dimensionality $d = 3$, Eq. (6) can be written in a more convenient form, such that

$$Q_c^{\min} = \left\{ (\beta_c)^{-1}, \alpha_c, Z_c, Y_c \right\} \quad (7)$$

where,

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

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

$$Z_c = \frac{p_c v_{\bar{p},c}}{k_B T_c} \quad (10)$$

$$Y_c = \gamma'_c \frac{T_c}{p_c} - 1 \quad (11)$$

define four scale factors: one energy scale unit $(\beta_c)^{-1}$, one length scale unit α_c , and two dimensionless *scale factors*

Z_c and Y_c characterizing two preferred directions across the critical point, along the critical isotherm and the critical isochore, respectively. α_c , which does not depend on the size $L \sim (V)^{\frac{1}{d}}$ of the container, has a clear physical meaning as length unit [36]: it represents the spatial extent of the short-ranged (Lennard-Jones like) molecular interaction [44], which allows us to define $v_{c,I} = \frac{k_B T_c}{p_c}$ as the volume of the microscopic *critical interaction cell* of each fluid. Z_c is the usual critical compression factor. Furthermore, $(Z_c)^{-1} = n_c v_{c,I}$ is the number of particles that fills $v_{c,I}$. n_c is the critical value of the number density $n = \frac{1}{v_p} = \frac{\rho}{m_p}$. Then the minimal set of data in Eq. (7) is related to the thermodynamic properties of the critical interaction cell of size $\alpha_c = (v_{c,I})^{\frac{1}{d}}$ [45].

We recall that the critical compression factor Z_c , and the critical Riedel factor $\alpha_{R,c}$ [46] [related to Y_c by $\alpha_{R,c} = Y_c + 1$], are among the basic parameters used to develop 4-CSEOS's for engineering fluid modeling [47].

The characteristic units $(\beta_c)^{-1}$ and α_c are the parameters needed to provide a dimensionless analysis of the fluid properties, leading to their canonical description based on the two-parameter corresponding state (2-CS) description. Obviously, the dimensionless form of the Sugden factor is given by

$$S_g^* = \frac{S_g}{(\alpha_c)^2} \quad (12)$$

Figure 2 (log-log scale) represents the confluent behavior of the rescaled dimensionless quantity $\frac{S_g^*}{|\Delta\tau^*|^\varphi}$ as a function of the dimensionless temperature distance $\Delta\tau^*$. Figure 2 complements Fig. 3 initially published by Moldover in Ref. [13], after normalization of the vertical axis by $(\alpha_c)^2$. Figure 2 illustrates the results of any classical two-parameter corresponding state theory (here the two characteristic parameters are $(\beta_c)^{-1}$ and α_c). Figure 2 shows the failure of the 2-CS principle in terms of molecular fluid complexity since, from xenon to water, the dimensionless Sugden factor covers one order of magnitude at the same reduced temperature distance to the critical point. Moreover, in terms of *classical* critical phenomena, using Eq. (1) where $\Delta\rho_{LV} \propto |\Delta\tau^*|^{\beta_{MF}}$ and $\sigma \propto |\Delta\tau^*|^{\phi_{MF}}$ with $\beta_{MF} = \frac{1}{2}$ and $\phi_{MF} = \frac{3}{2}$ [48], we obtain the *mean field* exponent $\varphi_{MF} = 1$. This mean-field value associated to the *classical* behavior of the correlation length (with exponent $\nu_{MF} = \frac{1}{2}$) expected from Van der Waals-like theories [48, 49], is unable to describe the experimental results, even at large temperature distance, as shown by the significantly positive slope $\varphi_{MF} - \varphi \simeq 0.065$ reported in Fig. 2. In addition, the scaling law $(d-1)\nu = \phi$, that explicitly involves d , is not correct for mean-field exponents for $d = 3$. We will turn back to the mean-field theories in § 4.2 when we will discuss the related classical-to-critical crossover description of the interfacial properties.

In the next step, the dimensionless scale factors Y_c and Z_c are introduced throughout the scale dilatation method

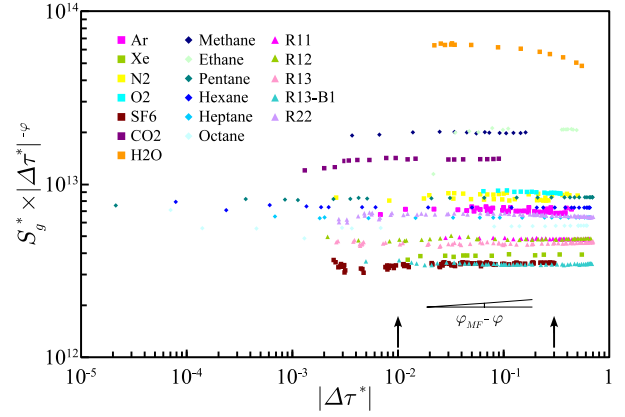


Figure 2: (Color online) Singular behavior (log-log scale) of the dimensionless quantity $\frac{S_g^*}{|\Delta\tau^*|^\varphi}$ as a function of the reduced temperature distance $|\Delta\tau^*|$, using α_c as a length unit and $(\beta_c)^{-1}$ as a energy unit, for eighteen nonhomogeneous one-component fluids (see Tables I and II). Each distinguishable curve illustrates the failure of the classical corresponding state scheme; The expected slope at large temperature distance for a *classical* power law with mean field exponent $\varphi_{MF} = 1$ is illustrated by the direction difference $\varphi_{MF} - \varphi$ (see text); The respective temperature distances $|\Delta\tau^*| = 10^{-2}$ and $|\Delta\tau^*| = 0.3$ are indicated by two arrows in lower horizontal axis (see text and caption of 1); Inserted Table gives the fluid color indexation.

[37]. Typically, the scale dilatation of the dimensionless temperature distance,

$$\Delta\tau^* = k_B \beta_c (T - T_c) \quad (13)$$

leads to the renormalized thermal field,

$$\mathcal{T}^* = Y_c \Delta\tau^* \quad (14)$$

The scale dilatation of the dimensionless order parameter density

$$\Delta m^* = (\alpha_c)^d (n - n_c) = (Z_c)^{-1} \Delta\tilde{\rho} \quad (15)$$

leads to the renormalized order parameter density

$$\mathcal{M}^* = (Z_c)^{\frac{d}{2}} \Delta m^* = (Z_c)^{\frac{1}{2}} \Delta\tilde{\rho} \quad (16)$$

where $\Delta\tilde{\rho} = \frac{\rho - \rho_c}{\rho_c}$. In addition, the renormalized form $\ell^* \equiv \xi^* = \frac{\xi}{\alpha_c}$ of the correlation length ξ [38], leads to the renormalized form, noted Σ^* , of the surface tension σ such that [50]

$$\Sigma^* \equiv \sigma^* = \sigma \beta_c (\alpha_c)^{d-1} \quad (17)$$

Taking into account Eqs. (1) and (12), the renormalized Sugden factor \mathcal{S}_g^* reads as follows [50]

$$\mathcal{S}_g^* = g^* (Z_c)^{-\frac{3}{2}} (\ell_{Ca}^*)^{d-1} = g^* (Z_c)^{-\frac{3}{2}} S_g^* \quad (18)$$

with $g^* = m_{\bar{p}}\beta_c\alpha_c g$. Therefore, after application of the scale dilatation method, the renormalized form of Eq. (1) is given by

$$S_{g^*}^* = \frac{\Sigma^*}{\mathcal{M}_{LV}^*} \quad (19)$$

where $\mathcal{M}_{LV}^* = (Z_c)^{\frac{d}{2}} (\alpha_c)^d \frac{n_L - n_V}{2} = (Z_c)^{\frac{1}{2}} \frac{\Delta\rho_{LV}}{2\rho_c}$ (n_L and n_V are the liquid number density and vapor number density on the VLE line, respectively). As expected [36], the collapse of all data on a master curve obtained from the scale transformations

$$\begin{aligned} \Delta\tau^* &\rightarrow T^* = Y_c \Delta\tau^* \\ S_g^* &\rightarrow S_{g^*}^* = g^* (Z_c)^{-\frac{3}{2}} S_g^* \quad (T1 \text{ case}) \\ &\rightarrow S_{g^*}^* \times |T^*|^{-\varphi} \quad (T2 \text{ case}) \end{aligned} \quad (20)$$

is shown in Figs. 3a (*T1 case*) and 3b (*T2 case*), *independently of any theoretical form used to represent this master behavior*. Now, the scatter of the collapsed data corresponds to the estimated precision (10%) for the Sugden factor of each fluid.

2.3. Predictive power of the scale dilatation method within the Ising-like preasymptotic domain

As initially shown in Ref. [37], we can expect to fit the master singular behavior of $S_{g^*}^*$ observed asymptotically close to the critical temperature by a *restricted* (two-term) Wegner-like expansion given by

$$S_{g^*}^* = \mathcal{Z}_S |T^*|^\varphi \left[1 + \mathcal{Z}_S^1 |T^*|^\Delta \right] \quad (21)$$

where $\varphi \approx 0.935$ and $\Delta \approx 0.51$ are the universal critical exponents, while \mathcal{Z}_S and \mathcal{Z}_S^1 are the master (i.e. unique) leading and confluent amplitudes, respectively, for all one-components fluids. By term-to-term comparison of Eqs. (4) and (21) using Eqs. (20), we obtain the following relations

$$\mathcal{Z}_S = g^* (\alpha_c)^{1-d} (Z_c)^{-\frac{3}{2}} (Y_c)^{-\varphi} S_0 \quad (22)$$

$$\mathcal{Z}_S^1 = (Y_c)^{-\Delta} S_1 \quad (23)$$

which shows the unequivocal link between master amplitudes and system-dependent amplitudes, through Q_c^{\min} [Eq. (7)].

In other words, only when the fluid-dependent set Q_c^{\min} and the master amplitudes \mathcal{Z}_S and \mathcal{Z}_S^1 are known, the restricted Wegner-like expansion [Eq. (4) with $i \leq 1$] of S_g can be determined for any one-component fluid by inverting Eqs. (22) and (23), i.e., $S_0 = (\alpha_c)^{d-1} (g^*)^{-1} (Z_c)^{\frac{3}{2}} (Y_c)^\varphi \mathcal{Z}_S$ and $S_1 = (Y_c)^\Delta \mathcal{Z}_S^1$. Then, the master values of \mathcal{Z}_S and \mathcal{Z}_S^1 conform to the universal features calculated for the Ising-like universality class (i.e., some combinations and ratios of \mathcal{Z}_S and \mathcal{Z}_S^1

take universal values, in agreement with the two-scale-factor universality). We will detail this point in § 4. Before, in the next Section, the scale transformations of Eq. (20) are shown to be in conformity with the asymptotic linearization [39] of the two relevant fields needed by the renormalization group theory. That leads indeed to the correct account for universal features estimated in the preasymptotic domain and the accurate determination of \mathcal{Z}_S using the present theoretical status provided by the massive renormalization scheme [9, 24].

3. ISING-LIKE CROSSOVER FUNCTIONS FOR THE SUGDEN FACTOR

To our knowledge, the theoretical function giving the classical-to-critical crossover of the interfacial tension $\sigma(\Delta\tau^*)$ is not available from the massive renormalization scheme, while the one of the coexisting density $\Delta\rho_{LV}(\Delta\tau^*)$ [25] remains affected by a large uncertainty on the value of the first confluent amplitude. Therefore, using either Eq. (1) for physical properties, or Eq. (19) for renormalized properties, the related crossover functions of the physical and renormalized Sugden factor remain undetermined from a theoretical point of view. Especially the value of \mathcal{Z}_S^1 [S_1 , respectively] in Eq. (21) [Eq. (4), respectively] cannot be estimated from theoretical prediction of the universal value of the confluent amplitude ratios related to the lowest confluent exponent Δ (see also our discussion in Section 4.1). However, *hyperscaling* related to the two-scale-factor universality of the asymptotic Ising-like description provides unambiguous determination of the values of \mathcal{Z}_S [S_0 , respectively] in Eq. (21) [Eq. (4), respectively]. This determination is presented below using the master forms of Ising-like crossover functions obtained from the massive renormalization scheme.

However, we note that a form equivalent to Eq. (21) was also recovered in the crossover approach of Belyakov et al [51], who used adjustable parameters as scale factors of the physical variables. The solution was obtained to first order in a ϵ -expansion (with $\epsilon = 4 - d$). It was not considered here due to the arbitrary adjustment to provide the crossover to a classical behavior.

3.1. Asymptotic hyperscaling description of the Sugden factor

It is well-established experimentally [12, 13] and theoretically [1, 52, 53, 55] that the asymptotic limit for $\Delta\tau^* \rightarrow 0$ of the product of the surface tension (σ) by the squared correlation length (ξ^2) takes a universal value, noted $R_{\sigma\xi}^\pm$, for the Ising-like universality class. This result corresponds to the Widom's scaling law between the corresponding critical exponents ν and ϕ given by

$$(d-1)\nu = \phi \quad (24)$$

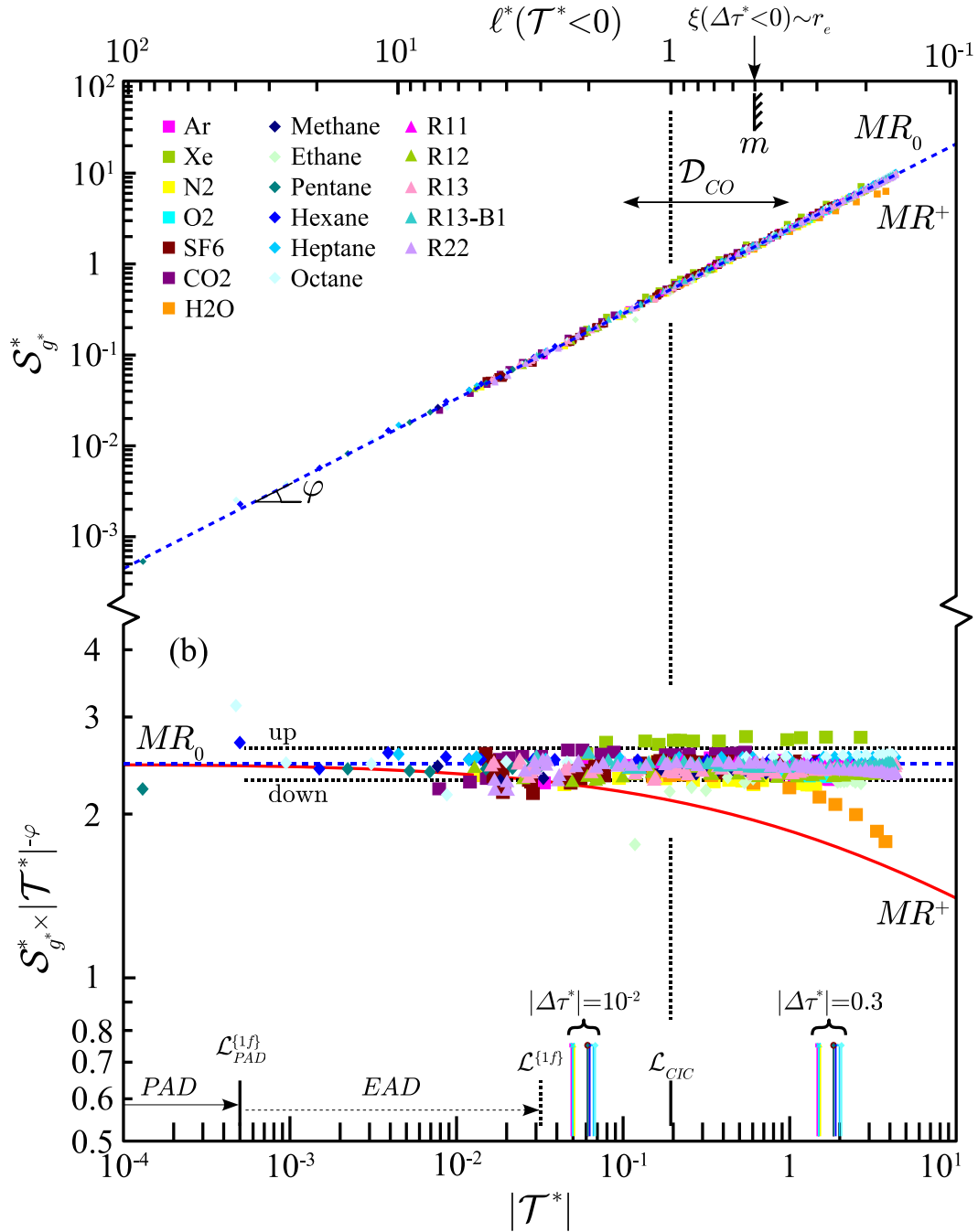


Figure 3: (Color online) a) Master singular behavior (log-log scale) of the renormalized Sugden factor $S_{g^*}^* = g^*(Z_c)^{-\frac{3}{2}} S_g^*$ (with $S_g^* = \frac{S_g}{(\alpha_c)^2}$ and $g^* = m_{\bar{p}} \beta_c \alpha_c g$), as a function of the renormalized thermal field $|T^*|$ [see text and Eq. (20)]; b) Master “confluent” behavior of the rescaled quantity $\frac{S_{g^*}^*}{|T^*|^{-\varphi}}$, as a function of the renormalized thermal field $|T^*|$ [see text and Eq. (20)]. In a) and b): The curves labeled MR_0 and MR^+ correspond to Eqs. (45) and (40), respectively [see text for the (up and down) dashed curves]; $\mathcal{L}_{PAD}^{\{1f\}}$ [Eq. (39)] and $\mathcal{L}^{\{1f\}}$ [Eq. (55)] correspond to the extension of the preasymptotic domain and the extended asymptotic domain, respectively; The graduation of the upper horizontal axis gives $\frac{\ell^*(T^* > 0)}{1.96}$ calculated from master crossover Eq. (32); See legend of 1a) The arrows in lower horizontal axis are related to $|\Delta\tau^*| = 10^{-2}$ and $|\Delta\tau^*| = 0.3$, respectively, using $|T^*| = Y_c |\Delta\tau^*|$ with Y_c given in Table II; Inserted Table gives the fluid color indexation.

with $d = 3$ in our present study. Therefore, we can introduce $R_{\sigma\xi}^{\pm}$ as follows

$$R_{\sigma\xi}^{\pm} = \beta_c \times \lim_{\Delta\tau^* \rightarrow 0^{\pm}} \left[\sigma (|\Delta\tau^*|) \times [\xi(\Delta\tau^*)]^{d-1} \right] \quad (25)$$

where the superscript \pm refers to the singular behavior of ξ above (+) or below (-) T_c . As a matter of fact, accounting for the universal ratio $\frac{\xi(\Delta\tau^* > 0)}{\xi(\Delta\tau^* < 0)} = 1.96$ for the Ising-like universality class [8], the amplitude combination $R_{\sigma\xi}^+ = (1.96)^{d-1} R_{\sigma\xi}^-$ shows that an interfacial property (here $\sigma \propto |\Delta\tau^*|^{\phi}$) in the non-homogeneous domain ($\Delta\tau^* < 0$) is related in a universal manner to the correlation length in the homogeneous domain ($\Delta\tau^* > 0$).

Considering the scaling law

$$d\nu = \gamma + 2\beta \quad (26)$$

it is also well-established that the amplitude combination $\left(\frac{\xi_0^+}{\alpha_c}\right)^{-d} \frac{\Gamma_0^+}{B^2}$, noted $\frac{R_C^+}{(R_{\xi}^+)^d}$, (using customary notations [7]) corresponds to the universal value of the asymptotic limit for $\Delta\tau^* \rightarrow 0$ of the following combination of singular properties

$$\frac{R_C^+}{(R_{\xi}^+)^d} = 4\beta_c (\rho_c)^2 \times \lim_{\Delta\tau^* \rightarrow 0^+} \left[\frac{\kappa_T(\Delta\tau^*) \times [\xi(\Delta\tau^*)]^{-d}}{[\Delta\rho_{LV}(\Delta\tau^*)]^2} \right] \quad (27)$$

Equation (27) relates the respective singular behaviors of the isothermal compressibility $\kappa_T(\Delta\tau^*)$ [with critical exponent γ and leading amplitude $\Gamma_0^+ = \frac{\Gamma_0^+}{\rho_c}$] in the homogeneous domain, the correlation length $\xi(\Delta\tau^*)$ [with critical exponent ν and leading amplitude ξ_0^+] in the homogeneous domain, and the order parameter density $\Delta\rho_{LV}(|\Delta\tau^*|)$ [with critical exponent β and leading amplitude $B_0 = 2\rho_c B$] in the non-homogeneous domain.

Using Eqs. (1), (25), and (27) to eliminate both properties $\sigma(|\Delta\tau^*|)$ and $\Delta\rho_{LV}(|\Delta\tau^*|)$, we obtain the following asymptotic equation

$$\lim_{|\Delta\tau^*| \rightarrow 0^-} [S_g]_{|\Delta\tau^*| \rightarrow 0^-} = R_{\sigma\xi}^+ \frac{(R_C^+)^{\frac{1}{2}}}{(R_{\xi}^+)^{\frac{3}{2}}} \times \frac{1}{2(\beta_c)^{\frac{3}{2}} \rho_c g} \times \lim_{\Delta\tau^* \rightarrow 0^+} \left[\frac{1}{[\kappa_T(\Delta\tau^*) \times \xi(\Delta\tau^*)]^{\frac{1}{2}}} \right] \quad (28)$$

which relates the asymptotical singular behavior of the Sugden factor in the nonhomogeneous domain to the ones of $\kappa_T(\Delta\tau^*)$ and $\xi(\Delta\tau^*)$ in the homogeneous domain. The corresponding scaling law reads

$$\left(\frac{d}{2} - 1\right) \nu = \varphi - \frac{\gamma}{2} \quad (29)$$

The scaling laws given by Eqs. (24), (26), and (29), where explicit reference to the space dimension is needed to connect correlation exponents and thermodynamic exponents, are characteristic of hyperscaling and reflect the universal features related to the two-scale-factor universality, which do not depend on the (homogeneous or non-homogeneous) domain (see also Ref. [56]).

3.2. The master crossover of the one-component fluid subclass

We are now able to construct a pseudo-crossover function based on Eq. (28). This pseudo-crossover function for the Sugden factor accounts exactly for the asymptotic two-scale factor universality but agrees only qualitatively with the one-parameter Ising-like critical crossover description at finite distance to the critical point. As a matter of fact, accurate expressions of the complete classical-to-critical crossover were recently proposed by Bagnuls and Bervillier [24] and written in appropriate Ising-like asymptotic forms by Garrabos and Bervillier [25] to account for error-bars associated with the estimations of the universal exponents near the non-Gaussian fixed point. Moreover, introducing only three characteristic numbers, $\mathbb{L}^{\{1f\}}$, $\Theta^{\{1f\}}$, and $\Psi^{\{1f\}}$ (see Ref. [35] for details), these crossover functions can be easily modified to accurately describe the master singular behavior of the one-component fluid subclass. In this description, two leading amplitudes \mathcal{Z}_{χ}^+ , \mathcal{Z}_{ξ}^+ , and one confluent amplitude, $\mathcal{Z}_{\chi}^{1,+}$ or $\mathcal{Z}_{\xi}^{1,+}$, can be selected as characteristic parameters of the Ising-like universal features observed in the Ising-like preasymptotic domain. \mathcal{Z}_{χ}^+ , \mathcal{Z}_{ξ}^+ , $\mathcal{Z}_{\chi}^{1,+}$, and $\mathcal{Z}_{\xi}^{1,+}$ are associated to the asymptotic crossover behavior of the correlation length and the susceptibility in the homogeneous domain. We recall that the corresponding master crossover functions are asymptotically approximated by the restricted (two terms) Wegner-like expansions given by the respective equations

$$\ell^*(T^*) = \mathcal{Z}_{\xi}^+(T^*)^{-\nu} \left[1 + \mathcal{Z}_{\xi}^{1,+}(T^*)^{\Delta} \right] \quad (30)$$

$$\varkappa^*(T^*) = \mathcal{Z}_{\chi}^+(T^*)^{-\gamma} \left[1 + \mathcal{Z}_{\chi}^{1,+}(T^*)^{\Delta} \right] \quad (31)$$

where $\mathcal{Z}_{\chi}^+ = 0.119$, $\mathcal{Z}_{\xi}^+ = 0.570$, $\mathcal{Z}_{\chi}^{1,+} = 0.555$ and $\mathcal{Z}_{\xi}^{1,+} = 0.377$ are the constant values of the master (i.e., fluid independent) amplitudes, with universal ratio $\frac{\mathcal{Z}_{\xi}^{1,+}}{\mathcal{Z}_{\chi}^{1,+}} = 0.68$ [9]. Accordingly, the modified crossover functions are given by the following equations

$$\frac{1}{\ell^*(T^*)} = \mathbb{Z}_{\xi}^{\{1f\}} \mathbb{Z}_{\xi}^+ t^{\nu} \times \prod_{i=1}^{i=3} [1 + X_{\xi,i} t^{D(t)}]^{Y_{\xi,i}} \quad (32)$$

$$\frac{1}{\varkappa^*(T^*)} = \mathbb{Z}_{\chi}^{\{1f\}} \mathbb{Z}_{\chi}^+ t^{\gamma} \times \prod_{i=1}^{i=3} [1 + X_{\chi,i} t^{D(t)}]^{Y_{\chi,i}} \quad (33)$$

with

$$D(t) = \frac{\Delta + \Delta_{MF} S_2 \sqrt{t}}{1 + S_2 \sqrt{t}} \quad (34)$$

(a)	exponent	Z_ξ^+	S_2	i	$X_{\xi,i}$	$Y_{\xi,i}$	(b)	exponent	Z_χ^+	S_2	i	$X_{\chi,i}$	$Y_{\chi,i}$
	$\nu = 0.6303875$	2.121008	22.9007	1	40.0606	-0.098968		$\gamma = 1.2395935$	3.709601	22.9007	1	29.1778	-0.178403
	$\Delta = 0.50189$			2	11.9321	-0.15391		$\Delta = 0.50189$			2	11.7625	-0.282241
	$\nu_{MF} = 0.5$			3	1.90235	-0.00789505		$\gamma_{MF} = 1.0$			3	2.05948	-0.0185424
					$Z_\xi^{1,+}$	5.81623						$Z_\chi^{1,+}$	8.56347

Table III: Values of the universal exponents and universal parameters for the crossover functions estimated in Ref. [25]; Part (a) correlation length case in the homogeneous domain; Part (b) susceptibility case in the homogeneous domain.

and

$$t = \Theta^{\{1f\}} \mathcal{T}^* \quad (35)$$

All critical exponents (ν , γ , Δ , Δ_{MF}) and constants (Z_ξ^+ , Z_χ^+ , $X_{\xi,i}$, $Y_{\xi,i}$, $X_{\chi,i}$, $Y_{\chi,i}$, S_2) of the initial crossover functions defined in Ref. [25] are reported in Table III. Furthermore, in Eqs. (32) and (33), the prefactors $Z_\xi^{\{1f\}}$ and $Z_\chi^{\{1f\}}$ relate the asymptotic master behavior given by Eqs. (30) and (31), respectively, and satisfy to unequivocal estimations from the three characteristic numbers $\mathbb{L}^{\{1f\}}$, $\Theta^{\{1f\}}$, and $\Psi^{\{1f\}}$ of the one-component fluid subclass [35], such that,

$$Z_\xi^{\{1f\}} = \left[Z_\xi^+ Z_\xi^+ \left(\Theta^{\{1f\}} \right)^\nu \right]^{-1} \equiv \mathbb{L}^{\{1f\}} \quad (36)$$

$$\begin{aligned} Z_\chi^{\{1f\}} &= \left[Z_\chi^+ Z_\chi^+ \left(\Theta^{\{1f\}} \right)^\gamma \right]^{-1} \\ &= \left[\left(\mathbb{L}^{\{1f\}} \right)^d \left(\Psi^{\{1f\}} \right)^2 \right]^{-1} \end{aligned} \quad (37)$$

The scale factor $\Theta^{\{1f\}}$ is defined from the following ratios of the confluent amplitudes

$$\Theta^{\{1f\}} = \left(\frac{Z_\xi^{1,+}}{Z_\xi^{1,+}} \right)^{\frac{1}{\Delta}} = \left(\frac{Z_\chi^{1,+}}{Z_\chi^{1,+}} \right)^{\frac{1}{\Delta}} \quad (38)$$

where $Z_\xi^{1,+} = -\sum_{i=1}^{i=3} X_{\xi,i} Y_{\xi,i}$ and $Z_\chi^{1,+} = -\sum_{i=1}^{i=3} X_{\chi,i} Y_{\chi,i}$, with $\frac{Z_\xi^{1,+}}{Z_\chi^{1,+}} = 0.68$ [25]. All the values of these master constants are shown in Table IV.

We also note that the master *prefactors* $Z_\xi^{\{1f\}}$ and $Z_\chi^{\{1f\}}$, like all the other prefactors which modify the initial crossover functions to account for master behavior of the renormalized fluid properties, take the same value above and below the critical temperature, while only two of them are characteristic of the pure fluid subclass. In addition, the single master *crossover parameter* $\Theta^{\{1f\}}$ is the same for any property along the critical isochore, above and below the critical temperature. As demonstrated in Refs. [25, 35], it is possible to define unambiguously the extension $\mathcal{T}^* \lesssim \mathcal{L}_{PAD}^{\{1f\}}$ of the preasymptotic domain where each master crossover function can

be approximated by its restricted (two-term) expansion. Using $\Theta^{\{1f\}}$ (see Table IV) we obtain

$$\mathcal{T}^* \lesssim \mathcal{L}_{PAD}^{\{1f\}} = \frac{\mathcal{L}_{PAD}^{Ising}}{\Theta^{\{1f\}}} = \frac{10^{-3}}{(S_2)^2 \Theta^{\{1f\}}} \approx 5 \cdot 10^{-4} \quad (39)$$

where $\mathcal{L}_{PAD}^{Ising} = \frac{10^{-3}}{(S_2)^2}$ is defined in Ref. [25].

After appropriate rescaling of the master form of each property included in Eq. (28), we define the following master quantity

$$\hat{\mathcal{S}}(\mathcal{T}^*) = R_{\sigma\xi}^+ \frac{(R_C^+)^{\frac{1}{2}}}{(R_\xi^+)^{\frac{d}{2}}} \left[\frac{1}{\mathcal{r}^*(\mathcal{T}^*)} \times \frac{1}{\ell^*(\mathcal{T}^*)} \right]^{\frac{1}{2}} \quad (40)$$

where the correlation length and the susceptibility are given by Eqs. (32) and (33), respectively. $\hat{\mathcal{S}}(\mathcal{T}^*)$ [Eq. (40)] is the pseudo-crossover function of the Sugden factor which accounts for the massive renormalization description of the classical-to-critical crossover, *in the homogeneous domain* (see the discussion in next section). The corresponding curves labeled MR^+ in Figs. 3a and 3b, confirm the perfect agreement with the master behavior of the one-component fluid subclass when the leading asymptotic term of $\hat{\mathcal{S}}(\mathcal{T}^*)$, with $\mathcal{T}^* > 0$, corresponds to the one of $\mathcal{S}_{g^*}(|\mathcal{T}^*|)$, with $\mathcal{T}^* < 0$, for $|\mathcal{T}^*| \equiv \mathcal{T}^* \rightarrow 0$, as shown below.

3.3. The master leading power law of the renormalized Sugden factor

In the preasymptotic domain defined by Eq. (39), the above formulation of the master singular behavior of $\hat{\mathcal{S}}(\mathcal{T}^*)$, can be approximated by a restricted (two term) expansion of equation

$$\hat{\mathcal{S}}(\mathcal{T}^*) = \mathcal{Z}_S |\mathcal{T}^*|^\varphi \left[1 + \hat{\mathcal{Z}}_S^{1,+} (\mathcal{T}^*)^\Delta \right] \quad (41)$$

where the decorated hat labels pseudo-physical quantities. Equation (41) contains the asymptotic constraint of Eq. (28), written following the master description

$$\lim \left[\hat{\mathcal{S}}(\mathcal{T}^*) \right]_{\mathcal{T}^* \rightarrow 0^+} = \lim \left[\mathcal{S}_{g^*}^*(|\mathcal{T}^*|) \right]_{\mathcal{T}^* \rightarrow 0^-} \quad (42)$$

where $\mathcal{S}_{g^*}^*(|\mathcal{T}^*|)$, with $\mathcal{T}^* < 0$, is given by Eq. (21), while the difference occurring to first order of the confluent

Correlation length	Susceptibility	
$\nu = 0.6303875$	$\gamma = 1.2396935$	
$(\mathbb{Z}_\xi^+)^{-1} = 0.471474$	$(\mathbb{Z}_\chi^+)^{-1} = 0.269571$	
$\mathcal{Z}_\xi^+ = \left[\mathbb{Z}_\xi^+ \mathbb{L}^{\{1f\}} (\Theta^{\{1f\}})^\nu \right]^{-1} = 0.57$	$\mathcal{Z}_\chi^+ = \left[\mathbb{Z}_\chi^+ (\mathbb{L}^{\{1f\}})^{-d} (\Psi^{\{1f\}})^{-2} (\Theta^{\{1f\}})^\gamma \right]^{-1} = 0.119$	$\Theta^{\{1f\}} = 4.288 \cdot 10^{-3}$
$\mathbb{Z}_\xi^{\{1f\}} \equiv \mathbb{L}^{\{1f\}} = 25.6988$	$\mathbb{Z}_\chi^{\{1f\}} = \left[(\mathbb{L}^{\{1f\}})^d (\Psi^{\{1f\}})^2 \right]^{-1} = 1950.7$	
$\Delta = 0.50189$		
$\mathbb{Z}_\xi^{1,+} = 0.68 \mathbb{Z}_\chi^{1,+} = 5.81623$	$\mathbb{Z}_\chi^{1,+} = 8.56347$	
$\mathcal{Z}_\xi^{1,+} = \mathbb{Z}_\xi^{1,+} (\Theta^{\{1f\}})^\Delta = 0.68 \mathcal{Z}_\chi^{1,+} = 0.377$	$\mathcal{Z}_\chi^{1,+} = \mathbb{Z}_\chi^{1,+} (\Theta^{\{1f\}})^\Delta = 0.555$	

Table IV: Universal and master constants of Eqs. (32) and (33) for the correlation length and the susceptibility, respectively, in the homogeneous domain (see text and Refs. [25, 35] for details). Upper part (lines 1 to 4) refers to the Ising-like leading term; The values of the three characteristic numbers of the one component fluid “subclass” are reported in column 3, that demonstrates the unequivocal relation between the “master” crossover functions [35] and the “MR” crossover functions [25], with prefactors given in line 5. Lower part (lines 6 to 8) refers to the first term of the confluent correction to scaling.

corrections to scaling is discussed below (see § 4.1). The leading amplitude \mathcal{Z}_S has the master form

$$\mathcal{Z}_S = R_{\sigma_\xi}^\pm \frac{(R_C^+)^{\frac{1}{2}}}{(R_\xi^+)^{\frac{d}{2}}} \left(\mathcal{Z}_\chi^+ \mathcal{Z}_\xi^+ \right)^{-\frac{1}{2}} \quad (43)$$

Using the universal values $R_{\sigma_\xi}^+ = 0.376 (\pm 0.017)$ [7, 12, 13, 55], $R_C^+ = 0.0574 (\pm 0.0020)$ [24], $R_\xi^+ = 0.2696 (\pm 0.0007)$ [24], estimated for the Ising-like universality class, and the values $\mathcal{Z}_\chi^+ = 0.119$, $\mathcal{Z}_\xi^+ = 0.57$ (see Table IV), we obtain

$$\mathcal{Z}_S = 2.47 (\pm 0.17) \quad (44)$$

We note that the error-bar reported for each universal amplitude combination only account for theoretical uncertainties on the estimated values of the universal combinations $R_{\sigma_\xi}^+$, R_C^+ , and R_ξ^+ , while the “best” central values of the master amplitudes \mathcal{Z}_χ^+ and \mathcal{Z}_ξ^+ are estimated using xenon as a standard one-component fluid. The large error-bar ($\pm 5\%$) on $R_{\sigma_\xi}^+$ accounts for the theoretical values $R_{\sigma_\xi}^+ \simeq 0.367 (\pm 0.009)$ and $R_{\sigma_\xi}^+ \simeq 0.372 (\pm 0.009)$ estimated by Zinn and Fisher [54] from numerical studies of three-dimensional Ising models, the (min and max central) values $R_{\sigma_\xi}^+ \simeq 0.36 (\pm 0.01)$ and $R_{\sigma_\xi}^+ \simeq 0.39 (\pm 0.03)$ quoted by Privman et al [7] on the basis of previous theoretical calculations, and the median values $R_{\sigma_\xi}^+ \simeq 0.386 (\pm 0.1)$ [13] and $R_{\sigma_\xi}^+ \simeq 0.381 (\pm 0.01)$ [12] which were initially obtained from the analysis of the experimental situation for fluids (see Refs. [11, 12, 14–22]).

The published data of the effective exponent-amplitude pair $\{\varphi_e; S_{0,e}\}$ reported in Table I (columns 3 & 4) allows one to validate this leading master description at *finite* distance to the critical point, using a method equivalent to the one proposed by Moldover [13] to estimate S_0 by averaging the values of $\frac{S_g}{|\Delta\tau^*|^{0.935}}$ in the vicinity

of $|\Delta\tau^*| = 0.01$. The corresponding Moldover’s values (noted $S_{0,\varphi}$ to recall for the use of the theoretical value $\varphi = 0.935$), are given in column 5 of Table I. In our present work, we have estimated $S_{0,\varphi}$ by the following relation $S_{0,\varphi} = S_{0,e} (0.01)^{\varphi_e - 0.935}$ (see also column 5, Table I). From these “measured” amplitude data at $|\Delta\tau^*| = 0.01$, the corresponding calculated values (column 6) of $\mathcal{Z}_{S,\varphi} = (\alpha_c)^{1-d} (g^*)^1 (Z_c)^{-\frac{3}{2}} (Y_c)^{-\varphi} S_{0,\varphi}$ [see Eq. (22)], are in close agreement with the asymptotic limit $\mathcal{Z}_S = 2.47$ estimated from above hyperscaling considerations. The mean value of the data reported in column 6 is $\langle \mathcal{Z}_{S,\varphi} \rangle = 2.450$. The residuals $\delta \mathcal{Z}_{S,\varphi}$ (column 7), expressed in %, are of the same order of magnitude ($\pm 3.1\%$) than the experimental uncertainty ($\pm 5\%$) [see for example the review of Moldover [13] for a detailed analysis of the experimental errors].

This *extended* master behavior is illustrated in Figs. 3a and 3b by the curve labeled MR_0 which corresponds to the pure power law of equation

$$S_{g^*}^* = \mathcal{Z}_S |T^*|^\varphi \quad (45)$$

where $\mathcal{Z}_S = 2.47$ [see Eq. (44)]. In Fig. 3b, the two lines labeled *up* [Eq. (44) with $\mathcal{Z}_S = 2.64$] and *down* [Eq. (44) with $\mathcal{Z}_S = 2.30$], respectively, account for the theoretical error-bar attached to this central value of \mathcal{Z}_S . Therefore, at least for a temperature range such that $|T^*| < 0.1$, all experimental results measured at finite temperature distance to the critical point lie in between these two lines. As noted previously, such a good agreement results from the “universal” median value $\varphi_e \equiv \varphi = 0.935$ of the effective exponent in the vicinity of $\Delta\tau^* = 0.01$. *De facto*, the asymptotical universal features can be observed in an extended asymptotic domain, since the confluent corrections to scaling attached to the exponent Δ

i) are only governed by the single scale factor Y_c whatever the singular property (as already shown for the correlation length, the susceptibility, and the order parameter density), and,

ii) are certainly very small in amplitude for the Sugden factor case. However, the present theoretical and experimental levels of uncertainties are of same order of magnitude and remain too high to provide an accurate estimation of the sign and amplitude of these (small) confluent corrections.

As our explicit Eq. (40) is restricted only to the universal features related to hyperscaling, there is a need for theoretical studies in the future to directly estimate the classical-to-critical crossover of the surface tension and Sugden factor in the non-homogeneous domain. Anticipating these investigations, the following discussion gives some complementary quantitative evaluations on the extended temperature range where the asymptotic leading power law of Eq. (45) can be correctly used to predict the Sugden factor behavior [since the applicability of the scale dilatation method goes far beyond that of the (un-correct) corresponding states principle].

4. DISCUSSION

4.1. Ising-like universal features within the preasymptotic domain

As demonstrated in Refs. [25, 35], each crossover function obtained from the massive renormalization scheme can be approximated by a restricted (two-term) Wegner-like expansion in the Ising-like preasymptotic domain which extends up to

$$|\mathcal{T}^*| \lesssim \mathcal{L}_{PAD}^{\{1f\}} = \frac{\mathcal{L}_{PAD}^{Ising}}{\Theta^{\{1f\}}} \simeq 5 \cdot 10^{-4}$$

(see the corresponding arrows in $|\mathcal{T}^*|$ axis of Figs. 3a and 3b). Therefore, in addition to Eq. (21) related to the master singular behavior of the renormalized Sugden factor, we are also interested in the following similar equations

$$\mathcal{M}_{LV}^* = \mathcal{Z}_M |\mathcal{T}^*|^\beta \left[1 + \mathcal{Z}_M^1 |\mathcal{T}^*|^\Delta \right] \quad (46)$$

$$\Sigma^* = \mathcal{Z}_\Sigma |\mathcal{T}^*|^\phi \left[1 + \mathcal{Z}_\Sigma^1 |\mathcal{T}^*|^\Delta \right] \quad (47)$$

related to the master singular behaviors of the renormalized order parameter density [see Eq. (16)] and renormalized surface tension [see Eq. (17)], respectively. Obviously, the hyperscaling law $d\nu = \gamma + 2\beta$ corresponds to the universal combination $\left(\mathcal{Z}_\xi^+\right)^{-d} \frac{\mathcal{Z}_\chi^+}{(\mathcal{Z}_M)^2} = R_C^+ \left(R_\xi^+\right)^d$, while Eq. (19) provides the “trivial” relation $\mathcal{Z}_S = \frac{\mathcal{Z}_\Sigma}{\mathcal{Z}_M}$. Both of these amplitude combinations relate unequivocally \mathcal{Z}_M and \mathcal{Z}_Σ to the selected characteristic leading amplitudes \mathcal{Z}_χ^+ and \mathcal{Z}_ξ^+ of the one-component fluid subclass. Alternatively, \mathcal{Z}_Σ and \mathcal{Z}_ξ^+ are unequivocally related by the universal amplitude combination $R_{\sigma\xi}^+ =$

$\mathcal{Z}_\Sigma \left(\mathcal{Z}_\xi^+\right)^{d-1}$. In such a case, we can also calculate the universal values $\mathcal{Z}_\Sigma = R_{\sigma\xi}^+ \left(\mathcal{Z}_\xi^+\right)^{d-1} = 1.750$ and $\mathcal{Z}_S = \frac{\mathcal{Z}_\Sigma}{\mathcal{Z}_M} = 1.867$ of the corresponding leading amplitudes for the respective crossover functions estimated in the massive renormalization scheme [with $\mathcal{Z}_\xi^+ = 2.121$, $\mathcal{Z}_\chi^+ = 3.7096$, and $\mathcal{Z}_M = \left(R_C^+ \mathcal{Z}_\chi^+\right)^{-\frac{1}{2}} \left(\frac{\mathcal{Z}_\xi^+}{R_\xi^+}\right)^{\frac{d}{2}} = 0.9375$; see Ref. [25] for detail]. Furthermore, in the relations [similar to Eqs. (32) and (33)] which define the master crossover functions for the order parameter density, the surface tension and the Sugden factor, the respective prefactors $\mathcal{Z}_M^{\{1f\}}$, $\mathcal{Z}_\Sigma^{\{1f\}}$, and $\mathcal{Z}_S^{\{1f\}}$ account for their unequivocal estimation only using the three characteristic numbers $\mathbb{L}^{\{1f\}}$, $\Theta^{\{1f\}}$, and $\Psi^{\{1f\}}$ of the one-component fluid subclass, such that,

$$\begin{aligned} \mathcal{Z}_M^{\{1f\}} &= \frac{\mathcal{Z}_M}{\mathcal{Z}_M (\Theta^{\{1f\}})^\beta} \\ &= \left(\mathbb{L}^{\{1f\}}\right)^d \Psi^{\{1f\}} \end{aligned} \quad (48)$$

$$\mathcal{Z}_\Sigma^{\{1f\}} = \frac{\mathcal{Z}_\Sigma}{\mathcal{Z}_\Sigma^+ (\Theta^{\{1f\}})^\phi} \equiv \left(\mathbb{L}^{\{1f\}}\right)^{d-1} \quad (49)$$

$$\begin{aligned} \mathcal{Z}_S^{\{1f\}} &= \frac{\mathcal{Z}_S}{\mathcal{Z}_S (\Theta^{\{1f\}})^\varphi} \\ &= \left[\mathbb{L}^{\{1f\}} \Psi^{\{1f\}}\right]^{-1} \end{aligned} \quad (50)$$

Equations (48) to (50) close the master representation of the singular behavior of the renormalized interfacial properties in the nonhomogeneous domain, in agreement with the two-scale factor universality of the Ising-like systems [see the corresponding values of the universal and master quantities reported in Table V].

Now, using Eq. (19) to compare the respective first confluent amplitudes of Eqs. (21), (47), (46), we obtain $\mathcal{Z}_S^1 = \mathcal{Z}_\Sigma^1 - \mathcal{Z}_M^1$. From Fig. 3b, because the asymptotic master singular behavior for S_{g^*} ($|\mathcal{T}^*|$) gives $\mathcal{Z}_S^1 \simeq 0$, we can expect the following universal values of the corresponding amplitude ratios

$$\begin{aligned} \frac{\mathcal{Z}_\Sigma^1}{\mathcal{Z}_M^1} &\simeq 1 \\ \frac{\mathcal{Z}_S^1}{\mathcal{Z}_M^1} &= 0.9 \frac{\mathcal{Z}_\Sigma^1}{\mathcal{Z}_\chi^{1,+}} \simeq 0 \end{aligned} \quad (51)$$

Such hypothesized “universal ratios” are consistent with Ising-like universal features of the asymptotic crossover estimated from the MR scheme, which are only characterized by a single confluent amplitude within the Ising-like preasymptotic domain. Here these universal features are preserved via the universal ratio value $\frac{\mathcal{Z}_M^1}{\mathcal{Z}_\chi^{1,+}} \simeq 0.9$, selecting $\mathcal{Z}_\chi^{1,+}$ as a characteristic confluent amplitude (see § 3.2 above). However, it is also important to note that this expected crossover must satisfy the scaling law $\varphi = \phi - \beta$ in the infinite limit $|\mathcal{T}^*| \rightarrow \infty$, which leads to the mean field

Order parameter density	Interfacial tension	Sugden factor
$\beta = 0.3257845$	$\phi = 2\nu = 1.260775$	$\varphi = \phi - \beta = 0.9349905$
$Z_M = (R_C^+ Z_\chi^+)^{-\frac{1}{2}} \left(\frac{Z_\xi^+}{R_\xi^+} \right)^{\frac{d}{2}} = 0.937528$	$Z_\Sigma = R_{\sigma\xi}^+ (Z_\xi^+)^{d-1} = 1.6915$	$Z_S = R_{\sigma\xi}^\pm \frac{(R_\xi^+)^{\frac{d}{2}}}{(R_C^+)^{\frac{1}{2}}} (Z_\chi^+ Z_\xi^+)^{\frac{1}{2}} = 1.8042$
$Z_M = Z_M (\mathbb{L}^{\{1f\}})^d \Psi^{\{1f\}} (\Theta^{\{1f\}})^\beta = 0.468$	$Z_\Sigma = Z_\Sigma (\mathbb{L}^{\{1f\}})^{d-1} (\Theta^{\{1f\}})^\phi = 1.1558$	$Z_S = Z_S \frac{(\Theta^{\{1f\}})^\varphi}{\mathbb{L}^{\{1f\}} \Psi^{\{1f\}}} = 2.47$
$Z_M^{\{1f\}} = (\mathbb{L}^{\{1f\}})^d \Psi^{\{1f\}} = 2.94878$	$Z_\Sigma^{\{1f\}} \equiv (\mathbb{L}^{\{1f\}})^{d-1} = 660.428$	$Z_S^{\{1f\}} = [\mathbb{L}^{\{1f\}} \Psi^{\{1f\}}]^{-1} = 223.634$
$\frac{(Z_\xi^{\{1f\}})^d}{Z_\chi^{\{1f\}} (Z_M^{\{1f\}})^2} = 1$	$\frac{Z_\Sigma^{\{1f\}}}{(Z_\xi^{\{1f\}})^{d-1}} = 1$	$\frac{Z_S^{\{1f\}}}{(Z_\xi^{\{1f\}} Z_\chi^{\{1f\}})^{\frac{1}{2}}} = 1$
$\Delta = 0.50189$		
$Z_M^1 = 0.9 Z_\chi^{1,+} = 7.70712$	$\frac{Z_\Sigma^1}{Z_\chi^{1,+}} (undefined)$	$\frac{Z_S^1}{Z_\chi^{1,+}} (undefined)$
$Z_M^1 = Z_M^1 (\Theta^{\{1f\}})^\Delta = 0.9 Z_\chi^{1,+} \approx 0.5$	$Z_\Sigma^1 \approx Z_M^1 \rightarrow \frac{Z_\Sigma^1}{Z_M^1} \approx 1$ (see Eq. 1) $\frac{Z_\Sigma^1}{Z_\chi^{1,+}} \approx 0.9 \rightarrow Z_\Sigma^1 \approx 0.5$	$Z_S^1 \approx 0$ (see Fig. 1) $\frac{Z_S^1}{Z_\chi^{1,+}} = 0.9 \frac{Z_S^1}{Z_M^1} \approx 0$

Table V: Universal and master constants for the order parameter density (column 1), the surface tension (column 2), and the Sugden factor (column 3), in the nonhomogeneous domain. Upper part (lines 2 to 5) refers to the Ising-like leading terms; The unity value of the combinations between the master prefactors reported in line 6 demonstrates that the asymptotic master crossover agrees with the two-scale-factor universality of the Ising-like systems. Lower part (lines 7 to 9) refers to the first term of the confluent correction to scaling (see text for detail).

value $\varphi_{MF} = 1$, using the mean-field values $\beta_{MF} = \frac{1}{2}$ and $\phi_{MF} = \frac{3}{2}$ [48]. In the range $|T^*| > 1$, the experimental results reported in Fig. 3a to 3b are in disagreement with such a mean-field prediction (see also below the § 4.3).

In addition, we note that the hyperscaling description using a pseudo-crossover function issued from singular properties in the homogeneous domain generates incorrect results in the complete temperature range, i.e., from the first-order contribution of Ising-like confluent exponent Δ until the leading contribution related to the mean-field exponent φ_{MF} .

For example, in our scheme based on the hyperscaling law $\varphi = \frac{\gamma+\nu}{2}$ [see Eq. (29)], the confluent amplitude $\hat{Z}_S^{1,+}$ in Eq. (41) can be made equal to $\hat{Z}_S^{1,+} = \frac{1}{2} (Z_\chi^{1,+} + Z_\xi^{1,+}) \approx 0.466$, leading to a universal ratio $\frac{\hat{Z}_S^{1,+}}{Z_\chi^{1,+}} = \frac{1}{2} \left(1 + \frac{Z_\xi^{1,+}}{Z_\chi^{1,+}} \right) \simeq 0.84$ which is different from zero.

Similarly, a description based only on the hyperscaling law $\varphi = 2\nu - \beta$ [see Eq. (24)] needs to replace the interfacial tension by the inverse squared correlation length in Eq. (19), and provides another pseudo-crossover function, given by the equation

$$\tilde{S}(|T^*|) = R_{\sigma\xi}^+ \times \frac{1}{\mathcal{M}_{LV}^*(|T^*|)} \times \left[\frac{1}{\ell^*(T^*)} \right]^2 \quad (52)$$

where the tilde is here to distinguish this equation from Eq. (40). In that case, a mixing occurs between properties in the homogeneous ($\ell^*(T^*)$) and non-homogeneous ($\mathcal{M}_{LV}^*(|T^*|)$) domains. In the Ising-like preasymptotic domain, accounting for the relation $Z_S = R_{\sigma\xi}^\pm Z_M (Z_\xi^+)^{-2}$, Eq. (52) can be approximated by

$$\tilde{S}(T^*) = Z_S (|T^*|)^\phi \left[1 + \tilde{Z}_S^1 (|T^*|)^\Delta \right] \quad (53)$$

In this latter scheme, the confluent amplitude \tilde{Z}_S^1 in Eq. (53) was estimated equal to $\tilde{Z}_S^1 = Z_M^1 + 2Z_\xi^{1,+} \approx 1.254$, leading to a universal ratio $\frac{\tilde{Z}_S^1}{Z_\chi^{1,+}} = 0.9 + 2\frac{Z_\xi^{1,+}}{Z_\chi^{1,+}} \simeq 2.26$ which is also significantly different from zero.

Looking now to the contribution of the leading term close to the Gaussian fixed point, our pseudo-crossover functions estimated above does not account for the appropriate mean-field-like description due to the failure of the two hyperscaling laws $\varphi = \frac{\gamma+\nu}{2}$ (which gives incorrect value $\varphi_{MF} = \frac{3}{4}$) and $\varphi = 2\nu - \beta$ (which gives incorrect value $\varphi_{MF} = \frac{1}{2}$) when we use the corresponding mean-field values $\gamma_{MF} = 1$, $\nu_{MF} = \frac{1}{2}$ and $\beta_{MF} = \frac{1}{2}$.

4.2. Ising-like master behavior in the extended asymptotic domain

In spite of the absence of accurate theoretical modelling for interfacial tension and Sugden factor along the VLE line, the massive renormalization description of the master crossover observed for the one-component fluid subclass can be used to provides a reasonable estimation of the renormalized correlation length in the nonhomogeneous domain, using the following equation

$$\ell^*(T^* < 0) = \frac{\ell^*(T^* > 0)}{1.96} \quad (54)$$

where $\ell^*(T^* > 0)$ of Eq. (32) is the renormalized correlation length in the homogeneous domain. Eq. (54) assumes that the universal ratio $\frac{\ell^*(T^* > 0)}{\ell^*(T^* < 0)} = 1.96$ is independent of the renormalized temperature like field. The result (for $T^* < 0$) is illustrated as a $\ell^*(T^* < 0)$ graduation of the upper horizontal axis of Figs. 3a and 3b. We

recall that ℓ^* gives the best estimate of the ratio $\frac{\xi}{\alpha_c}$ between the effective size (ξ) of the critical fluctuations and the effective size (α_c) of the attractive molecular interaction, the latter one being approximated by the range of the dispersion forces in Lennard-Jones-like fluids, which is slightly greater than twice the equilibrium distance r_e between two interacting particles of finite hard core size σ_{LJ} (thus $\alpha_c \approx 2r_e$, with $r_e \gtrsim \sigma_{LJ}$). Therefore, $\ell^* (|\mathcal{T}^*| = \mathcal{L}_{CIC}) \sim 1$ in the upper axis of Figs 3a and 3b is a rough estimate of the microscopic range of the molecular attractive interaction between fluid particles. Such a thermal field limit corresponds to the value $\mathcal{L}_{CIC} \approx 0.15$ (here the subscript *CIC* recalls that the extent of the short-ranged molecular interaction corresponds to the size of the critical interaction cell). Looking then at the “Ising-like” nature of $\mathcal{S}_{g^*} (|\mathcal{T}^*|)$, we observe in Figs. 3a and 3b a noticeable extension of the critical range associated to the condition $\ell^* (|\mathcal{T}^*|) \gtrsim 3$. Therefore, the extended asymptotic domain (labeled *EAD*) goes up to the limit

$$|\mathcal{T}^*| \lesssim \mathcal{L}^{\{1f\}} \approx 0.03 \quad (55)$$

(see the corresponding arrow noted $\mathcal{L}^{\{1f\}}$ in $|\mathcal{T}^*|$ axis). Within $|\mathcal{T}^*| \lesssim \mathcal{L}^{\{1f\}}$, the observed master behavior can be well-represented by $\mathcal{S}_{g^*} = \mathcal{Z}_S |\mathcal{T}^*|^\phi$ [see Eq. (45)], in conformity with the Ising-like universal features estimated from the massive renormalization scheme. We note that such Ising-like nature of \mathcal{S}_{g^*} in this extended $|\mathcal{T}^*|$ range complements in a self-consistent manner our previous analysis [57] of the master behavior of the renormalized order parameter density along the VLE line.

4.3. Non-critical behavior beyond the Ising-like extended asymptotic domain

In Ref. [57], it was observed for the xenon case, that the real crossover for the effective exponent β_e appears in the thermal field range $|\mathcal{D}_{CO}^*| \approx 0.1 - 1$ where $\ell^* (|\mathcal{T}^*|) \gtrsim 1$. We have illustrated this restricted range by a double arrow labeled \mathcal{D}_{CO} in Fig. 3a, where the upper x axis shows that the “large” values, i.e., $|\mathcal{T}^*| \geq 0.2$, of the renormalized thermal field correspond to $\frac{\ell^*(\mathcal{T}^* > 0)}{1.96} \lesssim 1$. For the value $\mathcal{L}_{CIC} \approx 0.15$ [lower axis of Fig. 3b], the condition $\ell^* (|\mathcal{T}^*| = \mathcal{L}_{CIC}) \sim 1$ [upper axis of Fig. 3a], corresponds to a rough estimate of the microscopic range of the molecular attractive interaction between fluid particles, as shown above in §4.2. Therefore, in terms of comparison between the correlation length and the range of the microscopic intermolecular interaction, the situation is similar to the one encountered in the homogeneous domain for the real crossover for the effective exponent γ_e [33]. Indeed, when $\ell^* (\mathcal{T}^* \leq 0) < 1$, any crossover function is not appropriate to account for the real non-universal behavior of the one-component fluids. We recall for example that $\ell^* (\mathcal{T}^* < 0) \cong \frac{\ell^*(\mathcal{T}^* > 0)}{1.96} \approx \frac{1}{2}$ (see the

limiting curve m in Fig. 3b) corresponds to a (non universal and non master) microscopic arrangement where the direct correlation distance between two interacting particles reaches the order of magnitude of the two particle equilibrium position r_e , i.e., $\xi (\Delta\tau^* < 0) \approx r_e$ (with $r_e \gtrsim \sigma_{LJ}$, where σ_{LJ} is the *size* of the particle). As previously noted in Ref. [57], the nonhomogeneous fluid is then made of coexisting gas and liquid which show significant differences in the averaged quantity of particles inside the critical interaction cell. Moreover, these differences increase upon approaching the triple point temperature, since the low density gas tends to behave as a perfect gas with one (i.e. non-interacting) particle within the volume of the critical interaction cell, while the condensed liquid tends to minimize the configuration energy of one particle by enclosing them in a particle cage made with an increasing number (up to twelve for the rare gas case) of the closest neighboring (repulsive) particles (i.e. the mean size d_{npc} of the neighboring particle cage is such that $r_e < d_{npc} \approx \sigma_{LJ}$). For such “low” and “high” local densities, cooperative density fluctuations in the nonhomogeneous domain have no physical sense at length scale larger than α_c and only the non-universal microscopic characteristics of each one-component fluid are involved in the thermodynamic properties, as clearly illustrated in Fig. 3b for the Sugden factor case by the significant increasing differences between the rescaled data for xenon and water in the range $|\mathcal{T}^*| > 0.2$ (or $\ell^* < 1$).

5. CONCLUSION

Examining a large set of experimental data, we have shown that the Sugden factor (or squared capillary length) of one-component fluids obeys a universal (master) singular behavior as a function of the distance to the critical temperature when these physical quantities are renormalized by the convenient, four fluid-dependent parameters, provided by the scale dilatation method. This master behavior can be related by hyperscaling to that of the renormalized correlation length of the density fluctuations and the renormalized isothermal susceptibility in the homogeneous domain. Using a previous analysis within a massive renormalization scheme in field theory of the two latter quantities, we show that the observed behavior of the Sugden factor is, to leading order, consistent with this theoretical prediction. The four critical coordinates which localize the gas-liquid critical point on the pressure, volume, temperature phase surface are then sufficient to estimate the four fluid-dependent parameters needed to calculate this asymptotic singular behavior of the Sugden factor. We also define the temperature range in renormalized units where this theoretical analysis holds practically, i.e., up to $|\mathcal{T}^*| \lesssim 0.03$ (or $\ell^* \lesssim 3$) in the nonhomogeneous domain. This range is similar to that for the renormalized order parameter which is related to the density difference between coexisting liquid and vapor. In a future work, we will show that this

master crossover behavior is useful to gain insight in the so-called parachor correlations (i.e., the surface tension

expressed as power law functions of the liquid-vapor density difference along the VLE line).

-
- [1] see for example, J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1984).
- [2] see for example, H.W. Xiang, *Corresponding States Principle and Practice: Thermodynamics, Transport and Surface Properties of fluids* (Elsevier, New York, 2005).
- [3] see for example, J. S. Rowlinson, *Liquids and Liquid mixtures* (Butterworths, London, 1971).
- [4] J. F. Ely and I. M. F. Marrucho, in *Equations of State for Fluids and Fluids Mixtures*, Part I, J. V. Sengers, R. F. Kayser, C. J. Peters, and H. J. White, Jr., Eds. (Elsevier, Amsterdam, 2000), pp. 289-320.
- [5] see for example, J. W. Leach, P. S. Chappellear, and T. W. Leland, *A. I. Ch. E. J.* **14**, 568 (1968) and references therein.
- [6] see for example, M. A. Anisimov and J. V. Sengers, in *Equations of State for Fluids and Fluids Mixtures*, Part I, J. V. Sengers, R. F. Kayser, C. J. Peters, and H. J. White, Jr., Eds. (Elsevier, Amsterdam, 2000), pp. 381-434.
- [7] V. Privman, P. C. Hohenberg, A. Aharony, in *Phase Transitions*, Vol. 14 (Academic Press, 1991) Chap.1.
- [8] J. Zinn-Justin, *Quantum Field Theory and Critical Phenomena*, 4th ed (Oxford University Press, 2002).
- [9] R. Guida and J. Zinn-Justin, *J. Phys. A: Math. Gen.* **31**, 8103 (1998).
- [10] S. Sugden, *J. Chem. Soc.* **168**, 38 (1924).
- [11] W. Rathjen and J. Straub, Proceedings of the 7th Symposium Thermophysical Properties ASME, 1977, pp. 839-850.
- [12] H. L. Gielen, O. B. Verbeke, and J. Thoen, *J. Chem. Phys.* **81**, 6154 (1984).
- [13] M. R. Moldover, *Phys. Rev. A* **31**, 1022 (1985).
- [14] M. Maass and C. H. Wright, *J. Am. Chem. Soc.* **43**, 1098 (1921).
- [15] C. L. Coffin and O. Maass, *J. Am. Chem. Soc.* **50**, 1427 (1928).
- [16] D. L. Katz and W. Saltman, *Ind. Eng. Chem.* **31**, 91 (1939).
- [17] D. Stansfield, *Proc. Phys. Soc. London*, **72**, 854 (1958).
- [18] B. L. Smith, P. R. Gardner, and E. H. C. Parker, *J. Chem. Phys.* **47**, 1148 (1967).
- [19] U. Grigull and J. Straub, in *Progress in Heat and Mass Transfer*, Vol. 2, edited by T. F. Irvine, Jr., W. E. Ibele, J. P. Hartnett, and R. J. Goldstein (Pergamon, New York, 1969) pp. 151-162.
- [20] W. Rathjen and J. Straub, *Wärme- und Stoffübertragung* **14**, 59 (1980).
- [21] J. Straub, N. Rosner, and U. Grigull, *Wärme- und Stoffübertragung* **13**, 241 (1980).
- [22] V. N. Vargaftik, L. D. Voljak, and B. N. Volkov, *J. Phys. Chem. Ref. Data*, **12**, 817 (1983).
- [23] F. J. Wegner, *Phys. Rev. B* **5**, 4529 (1972).
- [24] C. Bagnuls and C. Bervillier, *Phys. Rev. E* **65**, 066132 (2002).
- [25] Y. Garrabos and C. Bervillier, *Phys. Rev. E* **74**, 021113 (2006).
- [26] C. Bagnuls and C. Bervillier, *J. Phys. (France) - Lettres* **45**, L-95 (1984).
- [27] C. Bagnuls, C. Bervillier, and Y. Garrabos, *J. Phys. (France)- Lettres* **45**, L-127 (1984).
- [28] C. Bagnuls and C. Bervillier, *Phys. Rev. B* **32**, 7209 (1985).
- [29] C. Bagnuls, C. Bervillier, D. I. Meiron, and B.G. Nickel, *Phys. Rev. B* **35**, 3585 (1987); **65**, 149901(E) (2002).
- [30] B. Widom, *J. Chem Phys.* **43**, 3892 (1965); **43**, 3898 (1965).
- [31] S. Fisk and B. Widom, *J. Chem. Phys.* **50**, 3219 (1969).
- [32] D. Stauffer, M. Ferer, and M. Wortiss, *Phys. Rev. Lett.* **29**, 345 (1972).
- [33] Y. Garrabos, F. Palencia, C. Lecoutre, C. Erkey, and B. LeNeindre, *Phys. Rev. E* **73**, 026125 (2006).
- [34] Y. Garrabos, C. Lecoutre, F. Palencia, B. LeNeindre, and C. Erkey, preprint (2006) [see cond-mat/0512408].
- [35] Y. Garrabos, F. Palencia, C. Lecoutre, B. LeNeindre, and C. Erkey, preprint (2006).
- [36] Y. Garrabos, Thesis, University of Paris VI, 1982.
- [37] Y. Garrabos, *J. Phys. (Paris)* **46**, 281 (1985) [for an english version see cond-mat/0512347]; **47**, 197 (1986).
- [38] Y. Garrabos, *Phys. Rev. E* **74**, 056110 (2006).
- [39] K. G. Wilson, *Phys. Rev. B* **4**, 3174 (1971); K.G. Wilson and J. K. Kogut, *Phys. Rep. C* **12**, 75 (1974).
- [40] B. A. Grigoryev, B. V. Nemzer, D. S. Kurumov, and J. V. Sengers, *Int. J. Thermophys.* **13**, 453 (1992).
- [41] K. S. Pitzer, *J. Am. Chem. Soc.* **77**, 3427 (1955); K. S. Pitzer, D. Z. Lippmann, R. F. Curl, C. M. Huggins, and D. E. Patersen, *J. Am. Chem. Soc.* **77**, 3433 (1955); K. S. Pitzer and R. F. Curl, *J. Am. Chem. Soc.* **79**, 2369 (1957); K. S. Pitzer and G.O. Hultgren, *J. Am. Chem. Soc.* **80**, 4793 (1958); R. F. Curl and K. S. Pitzer, *Ind. Eng. Chem.* **50**, 265 (1958).
- [42] J.M.H. Levelt-Sengers and J. V. Sengers, in *Perspectives in Statistical Physics*, Edited by H. J. Raveché (North-Holland Pub. Comp., Amsterdam, 1981) pp. 241-271.
- [43] We admit that the molecular mass, $m_{\bar{p}}$, of each constitutive fluid particle is a known quantity, in order to infer N value from the total mass ($M = Nm_{\bar{p}}$) measurement of the amount of fluid matter filling the container of volume V (N is the total number of particles of the fluid system).
- [44] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (corrected edition), (Wiley, New York, 1964).
- [45] Y. Garrabos, *Preprint* 2005 [see cond-mat/0512408].
- [46] L. Riedel, *Chem Eng. Tech.* **26**, 83 (1954).
- [47] see for example, B. E. Poling, J. M. Prausnitz, and J. P. O'Connell, *The properties of gases and liquids*, 5th edition (McGraw Hill, New York, 2001).
- [48] B. Widom, *J. Phys. Chem.* **100**, 13190 (1996).
- [49] A. Kostrowicka Wyczalkowska, J. V. Sengers, and M. A. Anisimov, *Physica A* **334**, 482 (2004).
- [50] B. Le Neindre, Y. Garrabos, *Fluid Phase Equilib.* **198**, 165 (2002).
- [51] M. Y. Belyakov, S. B. Kiselev, and A. R. Muratov, *High Temp.* **33**, 701 (1995).
- [52] K. K. Mon, *Phys. Rev. Lett.* **60**, 2749 (1988).

- [53] L. J. Shaw and M. E. Fisher, Phys. Rev. **A39**, 2189 (1989).
- [54] S.-Y. Zinn and M. E. Fisher, Physica A **226**, 168 (1996).
- [55] M. E. Fisher and S.-Y. Zinn, J. Phys. A **31**, L629 (1998).
- [56] On a general point of view, the concept of two-scale-factor universality implies that the singular free energy density belonging to the volume ξ^d is a universal function of the single variable $\frac{h}{|t|^{\frac{d\nu\delta}{\delta+1}}}$. However, its practical formulation was currently made using the single variable $\frac{t}{|m|^\beta}$ on the path $h = 0$ (the critical isochore), mainly for easier comparison with experimental results.
- [57] Y. Garrabos, B. Le Neindre, R. Wunenburger, C. Lecoutre-Chabot, and D. Beysens, Int. J. Thermophys. **23**, 997 (2002).