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# Master singular behavior for the Sugden factor of the 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 Brosetta  
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.  
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We present the master (i.e. unique) behavior of the squared capillary length - so called the Sugden factor-, as a function of the temperature-like field along the critical isochore, asymptotically close to the gas-liquid critical point of 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 introduces the fluid-dependent scale factors in a manner analog with the linear relations between physical fields and scaling fields needed by the renormalization theory applied to the Ising-like universality class. The master behavior for the Sugden factor satisfies hyperscaling and 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".

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## 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 underground geological fluid flows 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's) 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 prin-

ciple [2, 3, 4]. In the following we call  $n$ -CSEOS such an EOS which contains  $n \geq 2$  system-dependent parameters. The main reason for the 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  $n$ -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  $\ell_{Ca}$ , 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 factor reflects the balance between interfacial and volumic forces which defines the shape and the position of the

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

interface in 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  $\sigma$  and the density difference  $\Delta\rho_{LV} = \rho_L - \rho_V$  between coexisting liquid (density  $\rho_L$ ) and vapor (density  $\rho_V$ ) phases by the equation

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

where  $\sigma$  is the surface tension. Therefore, the knowledge of the Sugden factor is an important challenge to provide better control on non homogeneous fluid properties.

In addition, as clearly documented two decades ago [11, 12, 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, 15, 16, 17, 18, 19, 20, 21, 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) 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, specially 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], specially 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 [26, 27, 28, 29], our main objective is to accurately estimate this leading asymptotic behavior of  $S_g$  from scaling arguments [1, 30, 31, 32] and available MR description [33, 34, 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, 37, 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 adjustable parameters*, 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 hyperscaling [1, 30, 31, 32] and MR description [26, 28, 29] of the critical crossover is reported in Section 3. The master leading

terms of the MR crossover functions for the correlation length and the susceptibility in the homogeneous domain [24, 25], are used to demonstrate that the fit of the master behavior observed in the (nonhomogeneous) extended asymptotic domain can be made with a theoretical precision of the same order of magnitude than the experimental one. 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-like range where this theoretical treatment becomes unappropriate 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, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 40].  $T$  ( $T_c$ ) is the temperature (critical temperature).  $S_g(|\Delta T|)$  data are 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  $T_{c,exp}$  is the measured (or estimated) critical temperature in the experiments [ $\rho$  ( $\rho_c$ ) is the density (critical density)]. The relative precision claimed by the authors is generally lower than 10%. For most fluids,  $S_g$  was fitted using the effective power law of equation [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  $\varphi_e$  considered as an adjustable parameter when measurements were performed in a restricted temperature range at finite distance to  $T_{c,exp}$ . The corresponding results  $\varphi_e; S_{0,e}$  [with free (or fixed) value of  $\varphi_e$ ] for each selected fluid are summarized in columns 3 and 4 of Table I (references are given in column 2). 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 these fitting analyses are:

i) the correlation between the effective values of  $S_{0,e}$  and  $\varphi_e$  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  $\varphi_e$  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  $\varphi = 2\nu - \beta = 0.935 \pm 0.015$  obtained from the present theoretical estimation of the critical exponents  $\nu =$  and  $\beta =$  [9] [see below Eq. (5)], appears consistent with the  $S_g$  data, whatever the one-component fluid.

ii) accordingly, the temperature dependence of the effective exponent over a larger temperature range is very small (then with a sign not unambiguously defined for the small amplitude of the leading confluent term), whatever the one-component fluid or the extension of the temperature range of the fit;

iii) the measured value of the effective exponent is never equal to the mean-field value  $\varphi_{MF} = 1$ , whatever the one-component fluid and even the large temperature range of the fit;

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 (CP), 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  $\sigma$  and  $\Delta\rho_{LV}$ , respectively, and  $\nu \approx 0.63$  is the universal value [9] of the critical exponent for the correlation length, 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, the asymptotic singular decrease of  $S_g$  must be fitted by the following equation

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

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 critical exponent

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

only takes its universal value  $\varphi \approx 0.935$  asymptotically when  $\Delta\tau^* \rightarrow 0$ . Therefore, the weak temperature dependence of the effective exponent at finite value of  $\Delta\tau^*$ , first 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).

To illustrate this behavior, the Sugden factor  $S_g \equiv (\ell_{Ca})^2$  (expressed in  $m^2$ ) can be divided by  $(T_c - T)^\varphi$  (expressed in  $K^\varphi$ , with  $\varphi = 0.935$ ) [13]. In Figure 1a (log-log scale), this convenient scaled form  $\frac{S_g}{(T_c - T)^\varphi} [m^2 K^{-\varphi}]$ , is shown as a function of the temperature distance  $T_c - T [K]$  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 use of such dimensional quantities 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, while the quasi-horizontal line whatever the fluid (except the water case which needs a special attention given in § 4.3) shows that the confluent contribution is negligible (i.e.  $\sum_{i=1}^{\infty} S_i (T_c)^{-i\Delta} (T_c - T)^{i\Delta} \sim 0$ ).  $S_g$  values at  $T_c - T = 1K$  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 [ $S_0(CH_4) = 13.80 mm^2$ ].

We have noted that some of the data reported in Fig. 1a have been measured in a large temperature range of the coexisting VLE line, including measurements close to  $T_{TP}$ . To separate the asymptotic critical range from the triple point location along the temperature axis, we have marked by vertical arrows the temperature distance where  $T = 0.7T_c$  (i.e. the temperature distance where the practical fluid-dependent acentric factor [41] is defined in the nonhomogeneous domain). The “non-critical” 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. Close to the critical point, the practical temperature range where the Wegner-like expansion fit the singular behavior does not usually exceed a few percent in  $|\Delta\tau^*|$  [42]. In a similar arbitrary manner, we have represented by vertical arrows the temperature distance where  $T = 0.99T_c$ , to make clear the “critical” temperature range  $T_c - T \leq 0.01T_c$  (the left hand side of the corresponding arrows in Fig. 1a), where the use of Eq. (4) has a theoretical justification, as discussed below in § 3. 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  $\mathcal{S}_{g^*}$ ) 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 (dimensionless)  $S_g^*$  [see below Eq. (12)] as a function of the (dimensionless) temperature field  $\Delta\tau^*$ ;

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

Fluid	Ref	$\varphi_e$	$S_{0,e}$ ( $mm^2$ )	$S_{0,\varphi}$ ( $mm^2$ )	Ref	$Z_{S,\varphi}$	$\delta Z_{S,\varphi}$ %
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 <sub>2</sub>	[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 <sub>2</sub>	[12]	0.909	4.85	5.47	This work	2.563	+4.6
CO <sub>2</sub>	[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 <sub>6</sub>	[11]	0.943	3.931	3.84	[13]	2.46	-0.4
CCl <sub>3</sub> F	[11]	0.928	6.234	6.44	This work	2.470	0.0
CCl <sub>2</sub> F <sub>2</sub>	[11]	0.936	5.615	5.589	This work	2.476	+0.3
CClF <sub>3</sub>	[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 <sub>3</sub>	[11]	0.938	3.879	3.826	This work	2.374	-3.1
CHClF <sub>2</sub>	[11]	0.937	6.859	6.796	This work	2.323	-6.0
C <sub>2</sub> H <sub>4</sub>	[14]			13.90	[13]	2.480	+0.4
CH <sub>4</sub>	[12]	0.933	13.6	13.73	This work	2.382	-3.6
C <sub>2</sub> H <sub>6</sub>	[14, 16]			14.42	[13]	2.437	-1.3
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	[15]			12.71	[13]	2.392	-3.2
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	[40]	0.935	12.916			2.488	+0.7
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	[40]	0.935	12.753			2.445	-1.0
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	[40]	0.935	12.520			2.552	+3.4
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	[40]	0.935	12.217			2.520	+2.0
H <sub>2</sub> O	[22]			34.72	[13]	2.262	-8.4
	[21]	0.91	33.2	37.25	This work	2.427	-1.7
$\langle Z_{S,\varphi} \rangle$						2.4530	$\pm 3.1$
$Z_S$						2.47	

Table I: Effective leading amplitude  $S_{0,e}$  [see Eq. (2)] of the Sugden factor  $S_g \equiv (\ell_{Ca})^2$  ( $\ell_{Ca}$  is the capillary length) (column 2) for several one-component fluids (column 1); Calculated values of the master amplitude  $Z_{S,e}$  (column 3) of the renormalized Sugden factor  $S_g^*$  [see Eq. (18)], using Eq. (22); The residual  $\delta Z_S = 100 \times \left( \frac{(Z_S)_{exp}}{Z_S} - 1 \right)$  (expressed in %) from the value  $Z_S = 2.47$  estimated from Eq. (43) is given in column 4; (for data sources and the selected fitting results see the references given in the last column).

## 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]. We recall only the main features (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  $\Phi_{a_{\bar{p}}}^p(p, v_{\bar{p}}, T) = 0$  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, 37, 38]. The critical data related to the fluids selected in Table I are reported in Table II. We note that  $T_c$  values of Table II, which were obtained from the thermodynamic analysis of the phase surface, can be slightly different from  $T_{c,exp}$  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  $d = 3$ , Eq. (6) can be written in a more convenient form, such that

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

which introduces the following four scale factors given by,

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

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

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

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

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

Equation (7) involves one energy scale unit  $(\beta_c)^{-1}$ , one length scale unit  $\alpha_c$ , and two dimensionless *scale factors*  $Z_c$  and  $Y_c$  characterizing two preferred directions to cross the critical point along the critical isotherm and the critical isochore, respectively.  $\alpha_c$ , which does not depend of 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* (CIC) 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  $v_{c,I}$ . 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  $\alpha_c$  are the parameters needed to provide a dimensionless analysis of the fluid properties, leading to their ‘‘classical’’ 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 1b (log-log scale; color online) 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 1b complements Fig. 3 initially published by Moldover in Ref. [13], after normalization of the vertical axis by  $(\alpha_c)^2$ . Figure 1b illustrates the results of any classical two-parameter corresponding state theory (here the two characteristic parameters are  $(\beta_c)^{-1}$  and  $\alpha_c$ ). Figure 1b, 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. 1b. In addition, the scaling law  $(d-1)\nu = \phi$ , that explicitly involve  $d$ , is not correct for mean-field exponents in three dimension. We will turn back on the mean-field theories in § 4.2 when we will discuss the related critical-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 [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

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

In addition, the renormalized form  $\ell^* \equiv \xi^* = \frac{\xi}{\alpha_c}$  of the correlation length  $\xi$  [38], leads to the renormalized form, noted  $\Sigma^*$ , of the surface tension  $\sigma$  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

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

As expected [36], the collapse on the master curve obtained from the scale transformations

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

is shown in Fig. 1c (*T1 case*) and 1d (*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  $\mathcal{S}_{g^*}^*$  observed asymptotically close to the critical temperature by a *restricted* (two-term) Wegner-like expansion given by

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

where  $\phi \approx 0.935$  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), such that  $S_0 = (\alpha_c)^{d-1} (g^*)^{-1} (Z_c)^{\frac{3}{2}} (Y_c)^\varphi \mathcal{Z}_S$  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 reported 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 MR 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

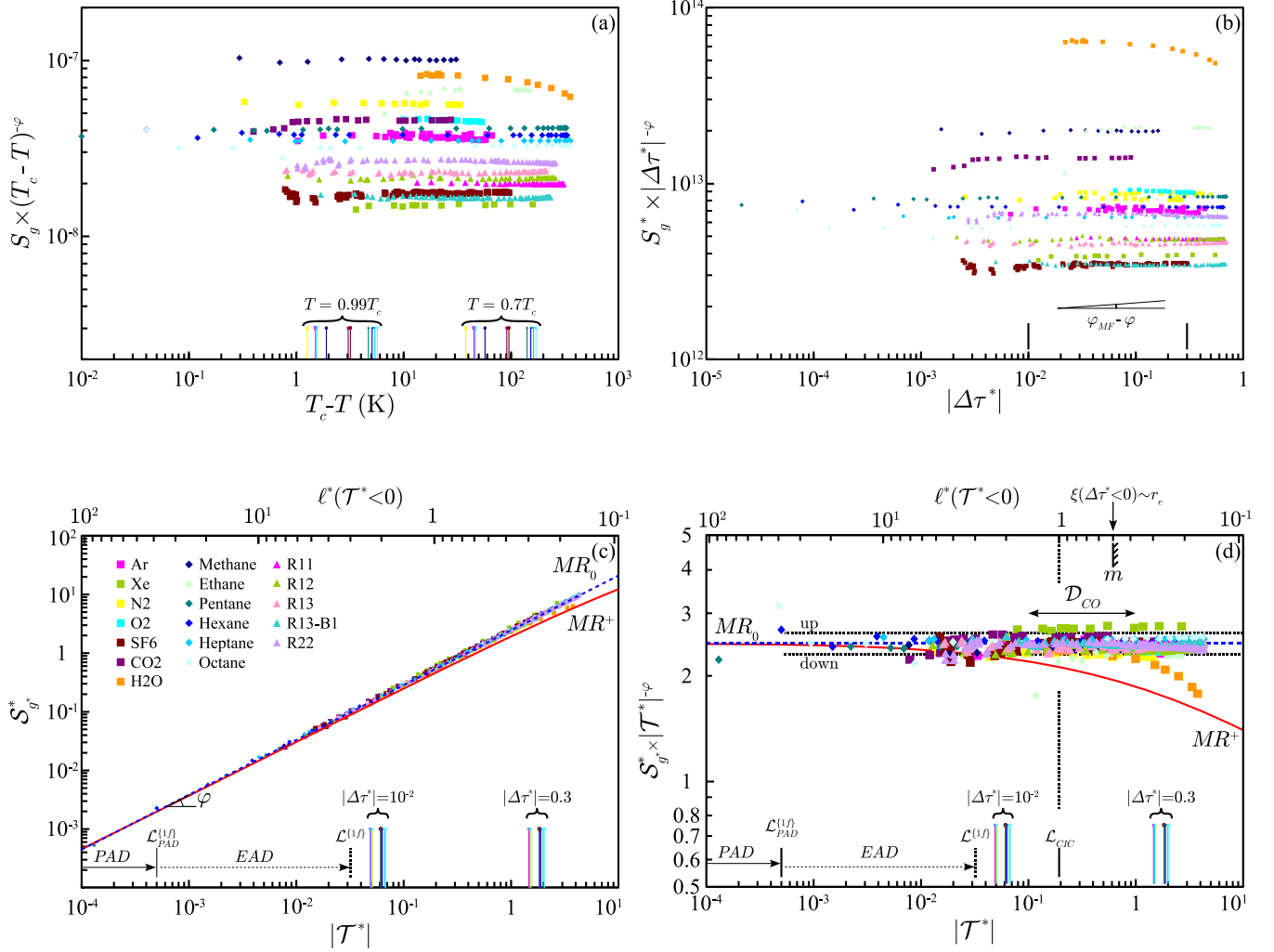


Figure 1: (Color online) a) Singular behavior (log-log scale) of  $\frac{S_g}{(T_c - T)^\varphi}$  (expressed in  $m^2 K^{-\varphi}$ , with  $\varphi = 0.935$ ), as a function of the temperature distance  $T_c - T$ , for nonhomogeneous one-component fluids (see Tables I and II). For each fluid, the arrows indicate the arbitrary temperature distances of  $T_c - T = 0.01T_c$  (left) and  $T_c - T = 0.3T_c$  (right); Inserted Table gives the color indexation for each fluid (see Table I and text for details); b) Log-Log scale of the respective dimensionless variables using  $\alpha_c$  as a length unit and  $(\beta_c)^{-1}$  as a energy unit. Each distinguishable curve illustrates the failure of the classical corresponding state scheme. The expected slopes of a *classical* power law with mean field exponent  $\varphi_{MF}$  are given by the directions labelled *MF* (see text); c) Master singular behavior (log-log scale) of the renormalized Sugden factor  $\mathcal{S}_{g^*} = g^* (Z_c)^{-\frac{3}{2}} S_g^*$  (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  $\mathcal{T}^* = Y_c |\Delta\tau^*|$  [see text and Eq. (20)]; d) Master “confluent” behavior of the rescaled quantity  $\frac{S_{g^*}}{|\mathcal{T}^*|^\varphi}$ , as a function of the renormalized thermal field  $\mathcal{T}^* = Y_c |\Delta\tau^*|$ , [see text and Eq. (20)]. In c) and d): The curve labelled  $MR^+$  corresponds to the Eq. (40) using crossover Eqs. (32) and (33) for the correlation length and the susceptibility, respectively, in the homogeneous domain;  $\mathcal{L}_{PAD}^{\{1f\}}$  [Eq. (39)] and  $\mathcal{L}^{\{1f\}}$  [see Eq. (55)] correspond to the extension of the preasymptotic domain and the extended asymptotic domain, respectively; The graduation of the upper horizontal axis gives  $\frac{\ell^*(\mathcal{T}^* > 0)}{1.96}$  calculated from master crossover Eq. (32); At large values of the renormalized thermal field ( $\mathcal{T}^* \geq 0.2$ ) which correspond to  $\frac{\ell^*(\mathcal{T}^* > 0)}{1.96} \lesssim 1$ , the restricted range labelled  $\mathcal{D}_{EC}$  indicates the effective crossover for the exponent  $\beta$ , while the vertical index labelled  $m$  gives a rough estimate of the *microscopic* limit  $\frac{\ell^*(\mathcal{T}^* > 0)}{1.96} \approx \frac{1}{2}$  where the correlation length  $\xi$  in the nonhomogeneous domain will reach the order of magnitude of the two particle equilibrium position  $r_e$  (with  $r_e \gtrsim \sigma$ , where  $\sigma$  is the *size* of the particle); See inserted Table and legend of a) for fluid color indexation; See legend of b) for arrows in lower horizontal axis.



$\sigma(\Delta\tau^*)$  is not available from the MR 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. Especially the value of  $Z_S^1$  [ $S_1$ , 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  $\Delta$  (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  $Z_S$  [ $S_0$ , 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 (MR) scheme.

However, we note that a form equivalent to Eq. (21) was also recovered in the crossover approach of Belyakov et al [51], who uses adjustable parameters as scale factors of the physical variables. The solution was obtained on the basis of the  $\epsilon$ -expansion in first order  $\epsilon$  and was not considered here due to the arbitrary of the phenomenological 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 interfacial tension by the squared correlation length takes a universal value, noted  $R_{\sigma\xi}^\pm$ , for the Ising-like universality class. This result proceeds from the Widom's scaling law between the corresponding critical exponents  $\nu$  and  $\mu$  given by

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

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

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

where the superscript  $\pm$  refers to the singular behavior of  $\xi$  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  $\left(\frac{\xi_0^+}{\alpha_c}\right)^{-d} \frac{\Gamma^+}{B^2}$ , 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

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

Equation (27) relates the singular behaviors of the correlation length  $\xi(\Delta\tau^*)$  [with critical exponent  $\nu$  and leading amplitude  $\xi_0^+$ ] in the homogeneous domain, the isothermal compressibility  $\kappa_T(\Delta\tau^*)$  [with critical exponent  $\gamma$  and leading amplitude  $\Gamma_0^+ = \frac{\Gamma^+}{p_c}$ ] in the homogeneous domain and the order parameter density  $\Delta\rho_{LV}(|\Delta\tau^*|)$  [with critical exponent  $\beta$  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  $\Delta\rho_{LV}(|\Delta\tau^*|)$  of nonhomogeneous domain, we obtain the following asymptotic equation

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

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 one 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 CP. 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 master description, two leading amplitudes  $\mathcal{Z}_\chi^+$ ,  $\mathcal{Z}_\xi^+$ , and one confluent amplitude among  $\mathcal{Z}_\chi^{1,+}$  and  $\mathcal{Z}_\xi^{1,+}$ , can be selected as characteristic parameters of the Ising-like universal features observed in the Ising-like preasymptotic domain.  $\mathcal{Z}_\chi^+$ ,  $\mathcal{Z}_\xi^+$ ,  $\mathcal{Z}_\chi^{1,+}$ , 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

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

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

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 the 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

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

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

with

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

and

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

All the critical exponents ( $\nu$ ,  $\gamma$ ,  $\Delta$ ,  $\Delta_{MF}$ ) and the constants ( $\mathbb{Z}_\xi^+$ ,  $\mathbb{Z}_\chi^+$ ,  $X_{\xi,i}$ ,  $Y_{\xi,i}$ ,  $X_{\chi,i}$ ,  $Y_{\chi,i}$ ,  $S_2$ ) of the initial crossover functions defined in Ref. [25] are reported in Table III. Furthermore, in Eqs. (32) and (33), the prefactors  $\mathbb{Z}_\xi^{\{1f\}}$  and  $\mathbb{Z}_\chi^{\{1f\}}$  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,

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

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

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

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

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

We also note that the master *prefactors*  $\mathbb{Z}_\xi^{\{1f\}}$  and  $\mathbb{Z}_\chi^{\{1f\}}$ , as all the other prefactors which modify the initial crossover functions to account for master behavior of the renormalized properties of the one-component fluid subclass, take the same value above and below the critical temperature, while only two of them are characteristic of this 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

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

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 Sughden factor which accounts for the MR description of the classical-to-critical crossover, in the homogeneous domain (see the discussion in next section). The corresponding curves labelled  $MR^+$  in Figs. 1c and 1d, confirm the perfect agreement with the master behavior of

(a)	exponent	$Z_\xi^+$	$S_2$	$i$	$X_{\xi,i}$	$Y_{\xi,i}$	(b)	exponent	$Z_\chi^+$	$S_2$	$i$	$X_{\chi,i}$	$Y_{\chi,i}$
	$\nu = 0.6303875$	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.

Correlation length	Susceptibility	
$\nu = 0.6303875$	$\gamma = 1.2396935$	
$(Z_\xi^+)^{-1} = 0.471474$	$(Z_\chi^+)^{-1} = 0.269571$	$\Theta^{\{1f\}} = 4.288 \cdot 10^{-3}$
$Z_\xi^+ = [Z_\xi^+ \mathbb{L}^{\{1f\}} (\Theta^{\{1f\}})^\nu]^{-1} = 0.57$	$Z_\chi^+ = [Z_\chi^+ (\mathbb{L}^{\{1f\}})^{-d} (\Psi^{\{1f\}})^{-2} (\Theta^{\{1f\}})^\gamma]^{-1} = 0.119$	$\Psi^{\{1f\}} = 1.74 \cdot 10^{-4}$
$Z_\xi^{\{1f\}} \equiv \mathbb{L}^{\{1f\}} = 25.6988$	$Z_\chi^{\{1f\}} = [(\mathbb{L}^{\{1f\}})^d (\Psi^{\{1f\}})^2]^{-1} = 1950.7$	$\mathbb{L}^{\{1f\}} = 25.6988$
$\Delta = 0.50189$		
$Z_\xi^{1,+} = 0.68 Z_\chi^{1,+} = 5.81623$	$Z_\chi^{1,+} = 8.56347$	
$Z_\xi^{1,+} = Z_\xi^{1,+} (\Theta^{\{1f\}})^\Delta = 0.68 Z_\chi^{1,+} = 0.377$	$Z_\chi^{1,+} = Z_\chi^{1,+} (\Theta^{\{1f\}})^\Delta = 0.555$	

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]. Lower part (lines 5 to 7) refers to the first term of the confluent correction to scaling.

the one-component fluid subclass when the asymptotic term of  $\hat{\mathcal{S}}(\mathcal{T}^*)$  corresponds to the one of  $\mathcal{S}_{g^*}^*(\mathcal{T}^*)$  for  $\mathcal{T}^* \rightarrow 0$ .

### 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  $\hat{\mathcal{S}}(\mathcal{T}^*)$ , with  $\mathcal{T}^* > 0$ , can be approximated by a restricted (two term) expansion of equation

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

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

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

where  $\mathcal{S}_{g^*}^*(|\mathcal{T}^*|)$ , with  $\mathcal{T}^* < 0$ , is given by Eq. (21), while the difference occurring to the first order of the confluent corrections to scaling is discussed below (see § 4.1). The leading amplitude  $\mathcal{Z}_S$  has the master form

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

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  $Z_\chi^+ = 0.119$ ,  $Z_\xi^+ = 0.57$  (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  $R_\xi^+$ , while the “best” central values of the master amplitudes  $Z_\chi^+$  and  $Z_\xi^+$  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, 15, 16, 17, 18, 19, 20, 21, 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  $Z_{S,\varphi} = (\alpha_c)^{1-d} (g^*)^1 (Z_c)^{-\frac{3}{2}} (Y_c)^{-\varphi} S_{0,\varphi}$  [see Eq. (22)], are in close agreement with the asymptotic limit  $Z_S = 2.47$  estimated from above hyperscaling considerations. The mean value of the data reported in column 6 is  $\langle Z_{S,\varphi} \rangle = 2.450$ . The residuals  $\delta Z_{S,\varphi}$  (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 realistic experimental errors].

This *extended* master behavior is illustrated in Figs. 1c and 1d by the curve labelled  $MR_0$  which corresponds to the pure power law of equation

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

where  $Z_S = 2.47$  [see Eq. (44)]. In Fig. 1d, the two lines labelled *up* [Eq. (44) with  $Z_S = 2.64$ ] and *down* [Eq. (44) with  $Z_S = 2.30$ ], respectively, account for the theoretical error-bar attached to this central value of  $Z_S$ . Therefore, at least for a temperature-like range such that  $|T^*| < 0.1$ , all the experimental results measured at finite temperature distance to the critical point appears “condensed” within these two lines. As noted previously, such a good agreement result 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  $\Delta$  are i) 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) certainly very small in amplitude for the Sudgen 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 the 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 the Sudgen factor in the non-homogeneous domain. Anticipating these investigations, the following discussion gives some complementary quantitative evaluations on the extended temperature-like range where the asymptotic leading power law of Eq. (45) can be correctly used to predict the Sudgen factor behavior (since the applica-

bility of the scale dilatation method goes far beyond the one of the invalid corresponding state 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 MR scheme can be approximated by a restricted (two term) Wegner-like expansion in the Ising-like preasymptotic domain which extends up to

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

(see the corresponding arrows in  $|T^*|$  axis of Fig. 1c and 1d). Therefore, in addition to Eq. (21) related to the master singular behavior of the renormalized Sudgen factor, we are also interested by the following similar equations

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

$$\Sigma^* = Z_\Sigma |T^*|^\mu \left[ 1 + Z_\Sigma^1 |T^*|^\Delta \right] \quad (47)$$

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  $d\nu = \gamma + 2\beta$  provides the universal combination  $\left( Z_\xi^+ \right)^{-d} \frac{Z_\chi^+}{(Z_M^+)^2} = R_C^+ \left( R_\xi^+ \right)^d$ , while Eq. (19) provides the “trivial” relation  $Z_S = \frac{Z_\Sigma}{Z_M}$ . Both of these amplitude combinations relate unequivocally  $Z_M$  and  $Z_\Sigma$  to the selected characteristic leading amplitudes  $Z_\chi^+$  and  $Z_\xi^+$  of the one-component fluid subclass. Alternatively,  $Z_\Sigma$  and  $Z_\xi^+$  are unequivocally related by the universal amplitude combination  $R_{\sigma\xi}^+ = Z_\Sigma \left( Z_\xi^+ \right)^{d-1}$ . In such a case, we can also calculate the universal values  $Z_\Sigma = R_{\sigma\xi}^+ \left( Z_\xi^+ \right)^{d-1} = 1.750$  and  $Z_S = \frac{Z_\Sigma}{Z_M} = 1.867$  of the corresponding leading amplitudes for the respective crossover functions estimated in the MR scheme [with  $Z_\xi^+ = 2.121$ ,  $Z_\chi^+ = 3.7096$ , and  $Z_M = \left( R_C^+ Z_\chi^+ \right)^{-\frac{1}{2}} \left( \frac{Z_\xi^+}{R_\xi^+} \right)^{\frac{d}{2}} = 0.9375$ ; 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 Sudgen factor, the respective prefactors  $Z_M^{\{1f\}}$ ,  $Z_\Sigma^{\{1f\}}$ , and  $Z_S^{\{1f\}}$  account for their unequivocal estimation only using the three characteristic numbers  $\mathbb{L}^{\{1f\}}$ ,  $\Theta^{\{1f\}}$ , and

Order parameter density	Interfacial tension	Sugden factor
$\beta = 0.3257845$	$\phi = 2\nu = 1.260775$	$\varphi = \phi - \beta = 0.9349905$
$\mathbb{Z}_M = (R_C^+ Z_\chi^+)^{-\frac{1}{2}} \left( \frac{Z_\xi^+}{R_\xi^+} \right)^{\frac{d}{2}} = 0.937528$	$Z_\Sigma = R_{\sigma\xi}^+ (Z_\xi^+)^{d-1} = 1.6915$	$Z_S = R_{\sigma\xi}^\pm \frac{(R_\xi^+)^{\frac{d}{2}}}{(R_C^+)^{\frac{1}{2}}} (Z_\chi^+ Z_\xi^+)^{\frac{1}{2}} = 1.8042$
$\mathcal{Z}_M = \mathbb{Z}_M (\mathbb{L}^{\{1f\}})^d \Psi^{\{1f\}} (\Theta^{\{1f\}})^\beta = 0.468$	$\mathcal{Z}_\Sigma = Z_\Sigma (\mathbb{L}^{\{1f\}})^{d-1} (\Theta^{\{1f\}})^\phi = 1.1558$	$\mathcal{Z}_S = Z_S \frac{(\Theta^{\{1f\}})^\varphi}{(\mathbb{L}^{\{1f\}} \Psi^{\{1f\}})^{\frac{1}{2}}} = 2.47$
$\mathbb{Z}_M^{\{1f\}} = (\mathbb{L}^{\{1f\}})^d \Psi^{\{1f\}} = 2.94878$	$\mathbb{Z}_\Sigma^{\{1f\}} \equiv (\mathbb{L}^{\{1f\}})^{d-1} = 660.428$	$\mathbb{Z}_S^{\{1f\}} = [\mathbb{L}^{\{1f\}} \Psi^{\{1f\}}]^{-1} = 223.634$
$\frac{(Z_\xi^{\{1f\}})^d}{Z_\chi^{\{1f\}} (Z_M^{\{1f\}})^2} = 1$	$\frac{Z_\Sigma^{\{1f\}}}{(Z_\xi^{\{1f\}})^{d-1}} = 1$	$\frac{Z_S^{\{1f\}}}{(Z_\xi^{\{1f\}} Z_\chi^{\{1f\}})^{\frac{1}{2}}} = 1$
$\Delta = 0.50189$		
$Z_M^1 = 0.9 Z_\chi^{1,+} = 7.70712$	$\frac{Z_\Sigma^1}{Z_\chi^{1,+}} (?)$	$\frac{Z_S^1}{Z_\chi^{1,+}} (?)$
$\mathcal{Z}_M^1 = Z_M^1 (\Theta^{\{1f\}})^\Delta = 0.9 \mathcal{Z}_\chi^{1,+} \approx 0.5$	$\mathcal{Z}_\Sigma^1 \approx \mathcal{Z}_M^1 \rightarrow \frac{Z_\Sigma^1}{Z_M^1} \approx 1$ (see Eq. 1) $\frac{Z_\Sigma^1}{Z_\chi^{1,+}} \approx 0.9 \rightarrow \mathcal{Z}_\Sigma^1 \approx 0.5$	$\mathcal{Z}_S^1 \approx 0$ (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 6) refers to the Ising-like leading term; The unity value of the combinations between the master prefactors reported in line 5 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).

$\Psi^{\{1f\}}$  of the one-component fluid subclass, such that,

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

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

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

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. 1d, the asymptotic master singular behavior expected for  $\mathcal{S}_g^*(|T^*|)$  is compatible with the following universal values of the corresponding amplitude ratios

$$\begin{aligned} \frac{Z_\Sigma^1}{Z_M^1} &\simeq 1 \\ \frac{Z_S^1}{Z_M^1} &= 0.9 \frac{Z_S^1}{Z_\chi^{1,+}} \simeq 0 \end{aligned} \quad (51)$$

Such hypothesized ‘‘universal ratios’’ of Eq. (51) 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  $\frac{Z_M^1}{Z_\chi^{1,+}} \simeq 0.9$ , 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  $|T^*| \rightarrow \infty$ , which leads to the mean field value  $\varphi_{MF} = 1$ , using the mean-field values  $\beta_{MF} = \frac{1}{2}$  and  $\phi_{MF} = \frac{3}{2}$  [48]. In the range  $|T^*| > \infty$ , the experimental results reported in Fig. 1a to 1d 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 uncorrect results in the complete temperature range, i.e. from the first-order contribution of Ising-like confluent exponent  $\Delta$  until the leading contribution related to the mean-field exponent  $\varphi_{MF}$ .

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

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

where the decorated tilde distinguishes new pseudo-

physical quantities from those of Eq. (40). In that case, a mixing occurs between properties in the homogeneous ( $\ell^*(\mathcal{T}^*)$ ) and nonhomogeneous ( $\mathcal{M}_{LV}^*(|\mathcal{T}^*|)$ ) domains. In the Ising-like preasymptotic domain, accounting for the relation with  $\mathcal{Z}_S = R_{\sigma\xi}^\pm \mathcal{Z}_M (\mathcal{Z}_\xi^+)^{-2}$ , Eq. (52) can be approximated by

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

In this latter scheme, the confluent amplitude  $\tilde{\mathcal{Z}}_S^1$  in Eq. (53) was estimated equal to  $\tilde{\mathcal{Z}}_S^1 = \mathcal{Z}_M^1 + 2\mathcal{Z}_\xi^{1,+} \approx 1.254$ , leading to a universal ratio  $\frac{\tilde{\mathcal{Z}}_S^1}{\mathcal{Z}_M^1} = 0.9 + 2\frac{\mathcal{Z}_\xi^{1,+}}{\mathcal{Z}_M^1} \simeq 2.26$  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 uncorrect value  $\varphi_{MF} = \frac{3}{4}$ ) and  $\varphi = 2\nu - \beta$  (which gives uncorrect 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 MR 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

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

where  $\ell^*(\mathcal{T}^* > 0)$  of Eq. (32) is the renormalized correlation length in the homogeneous domain. Eq. (54) assumes that the universal ratio  $\frac{\ell^*(\mathcal{T}^* > 0)}{\ell^*(\mathcal{T}^* < 0)} = 1.96$  is independent of the renormalized temperature like field. The result (for  $\mathcal{T}^* < 0$ ) is illustrated as a  $\ell^*(\mathcal{T}^* < 0)$  graduation of the upper horizontal axis of Figs. 1c and 1d. We recall that  $\ell^*$  gives the best estimate of the ratio  $\frac{\xi}{\alpha_c}$  between the effective size ( $\xi$ ) of the critical fluctuations and the effective size ( $\alpha_c$ ) of the attractive molecular interaction, the latter one being approximated by the dispersion forces in Lennard-Jones-like fluids which extend over a short range slightly greater than twice the equilibrium distance  $r_e$  between two interacting particles of finite hard core size  $\sigma$  (thus  $\alpha_c \approx 2r_e$ , with  $r_e \gtrsim \sigma$ ). Therefore,  $\ell^*(|\mathcal{T}^*| = \mathcal{L}_{CIC}) \sim 1$  in the upper axis of Figs 1c and 1d 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* recall that the effective extend of the short-ranged molecular interaction corresponds to the size of the critical interaction cell). Looking then to the “Ising-like” nature of  $\mathcal{S}_{g^*}^*(|\mathcal{T}^*|)$ , we observe in Figs. 1c and 1d a noticeable extension of the critical range associated to the condition  $\ell^*(|\mathcal{T}^*|) \gtrsim 3$ . Therefore, the extended asymptotic domain (labelled *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 MR 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  $\beta_e$  appears in the thermal field range  $|\mathcal{D}_{CO}^*| \approx 0.1 - 1$  where  $\ell^*(|\mathcal{T}^*|) \gtrsim 1$  (see Fig. 1d). 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  $\gamma_e$  [33]. Indeed, when  $\ell^* < 1$ , any MR crossover function is not appropriate to account for the real non-universal behavior of the one-component fluids. We recall for example that  $\ell^* \simeq \frac{1}{2}$  (see the limiting curve *m* in Fig. 1d) corresponds to a (non-master) microscopic arrangement where the direct correlation distance between two interacting particles is  $\approx r_e$  (i.e.,  $\xi(\Delta\tau^* < 0) \approx r_e \gtrsim \sigma$ ). 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 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 CIC volume, 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 rare gas case) of the closest neighboring (repulsive) particles (i.e. the mean size  $d$  of the cage is such that  $r_e < d \approx \sigma$ ). For such “low” and “high” local densities, cooperative density fluctuations have no physical sense at length scale larger than  $\alpha_c$  and the non-universal characteristics of each fluid are only involved in the thermodynamic properties, as clearly illustrated in Fig. 1d for the Sugden factor case by the significative increasing

differences between the rescaled data for xenon and water in the range  $|T^*| > 0.2$ .

## 5. CONCLUSION

We have provided an asymptotic description of the singular behavior of the renormalized Sugden factor (i.e.

the renormalized squared capillary length) of the one-component fluid subclass. This master crossover behavior can be observed up to  $|T^*| \approx 0.03$  (or  $\ell^* \approx 3$ ) in the non-homogeneous domain, as already noted for the renormalized order parameter density. In a future work, we will show that this master crossover behavior can be useful to estimate the parachor correlation along the VLE line.

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