

Universality of critical behavior in gases

J. M. H. Levelt Sengers*

Instituut voor Theoretische Fysica, Universiteit van Amsterdam, Amsterdam, Nederland

J. V. Sengers†

Laboratorium voor Technische Natuurkunde, Technische Hogeschool, Delft, Nederland

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P-V-T data in the critical region of six fluids (³He, ⁴He, Xe, O₂, CO₂, and H₂O) have been analyzed in terms of two scaled equations of state using the methods of statistical analysis. The results confirm the hypothesis of universality of critical behavior for these gases to within the current experimental accuracy. The results also support the validity of hyperscaling relations between thermodynamic and correlation function exponents for gases. Using the hypothesis of universality we then present critical-region parameters for fourteen fluids in terms of a universal equation of state.

I. INTRODUCTION

The hypothesis of universality of critical behavior asserts that in the vicinity of a critical point all systems belonging to a universality class obey the same scaled equation of state apart from only two adjustable reduction factors.^{1,2} For lattice models the principle of universality has been confirmed theoretically by the renormalization theory of critical phenomena.^{3,4} Experimental tests of the hypothesis of universality have been reported for a number of magnetic systems.^{5,6}

Since lattice models yield a rather artificial picture of the gas-liquid phase transition in fluids, the question whether different fluids belong to the same universality class cannot yet be answered *a priori*. However, the available experimental material can be tested as to the plausibility of such a universality hypothesis for fluids. We have made such a test by conducting a detailed statistical analysis of the experimental data for six different fluids, namely ³He, ⁴He, Xe, O₂, CO₂, and H₂O. The method of analysis is described in Sec. II and the results are reported in Sec. III. The experimental data analyzed correspond to a range $|\Delta\rho^*| \leq 0.25$ in reduced density $\Delta\rho^* = (\rho - \rho_c)/\rho_c$ and a range $10^{-4} \leq |\Delta T^*| \leq 3 \times 10^{-2}$ in reduced temperature $\Delta T^* = (T - T_c)/T_c$. We conclude that for the data of these six fluids the hypothesis of universality is valid within error, thus confirming earlier expectations.^{7,8} The "best" values for the universal critical exponents, however, differ from those for the three-dimensional Ising model.

Closely related with the hypothesis of universality are the postulated hyperscaling relations between the thermodynamic critical exponents and the critical exponents that characterize the anomalous behavior of the correlation function.^{9,10} The fact that the fluids do not seem to fall in the same

universality class as the Ising model makes it all the more urgent to investigate the validity of the hyperscaling relations for fluids. In Sec. IV we show that the available experimental results for fluids obey these relations.

Assuming the validity of the hypothesis of universality for fluids, we present in Sec. V parameters for a universal scaled equation of state in the critical region of 14 fluids. These parameters should be useful in describing the equation of state, compressibility, and density profiles of these fluids in the ranges of density and temperature specified above.

II. METHOD OF ANALYSIS

Scaled equations of state for the reduced chemical potential $\Delta\mu^* = [\mu(\rho, T) - \mu(\rho_c, T)]\rho_c/P_c$ in the vicinity of the gas-liquid critical point can be brought into the form¹¹

$$\frac{\Delta\mu^*}{\Delta\rho^*|\Delta\rho^*|^{\delta-1}} = Dh(y), \quad y = \frac{x}{x_0}, \quad (1a)$$

$$x = \frac{\Delta T^*}{|\Delta\rho^*|^{1/\beta}}. \quad (1b)$$

In addition to the critical pressure P_c , critical density ρ_c , critical temperature T_c , and the critical exponents β and δ , this equation contains at least two free parameters, namely D and x_0 . The critical exponent α for the constant-volume specific heat and the critical exponent γ for the isothermal compressibility are related to the exponents β and δ by the exponent relations

$$\alpha = 2 - \beta(\delta + 1), \quad (2a)$$

$$\gamma = \beta(\delta - 1). \quad (2b)$$

The coefficient D in (1a) is the amplitude of the power law for the critical isotherm so that $h(0)$

= 1. The parameter x_0 is chosen such that $y = -1$ along the coexistence curve. According to the hypothesis of universality, the critical exponents and also the function $h(y)$ would be the same for all gases; only the two scale factors D and x_0 would vary from substance to substance.^{2,8}

For magnetic systems one can devise a form of the scaling function $h(y)$ from the theoretical results for the Ising or Heisenberg models.^{5,12} For fluids we have evidence that the critical exponents differ from those of the Ising model, and we need to resort to phenomenological equations.

For the purpose of our analysis we used two representations of the scaled equations of state. The first is an equation proposed by Vicentini-Misoni *et al.*¹³ which we refer to as the MSLG equation:

$$\frac{\Delta\mu^*}{\Delta\rho^*|\Delta\rho^*|^{6-\beta}} = D(1+y) \left(\frac{1+E_2(1+y)^{2\beta}}{1+E_2} \right)^{(\gamma-1)/2\beta} \quad (3)$$

The equation contains one extra free parameter E_2 , in addition to x_0 and D . For convenience, we introduce a coefficient E_1 such that

$$E_1 = D/(1+E_2)^{(\gamma-1)/2\beta} \quad (4)$$

The second equation is the linear-model parametric equation proposed by Schofield¹⁴:

$$\begin{aligned} \Delta\mu^* &= r^{\beta\delta} a \theta (1 - \theta^2), \\ \Delta\rho^* &= r^{\beta} k \theta, \\ \Delta T^* &= r(1 - b^2 \theta^2), \end{aligned} \quad (5)$$

which also contains three free parameters, namely a , k , and b . They are related to the parameters D and x_0 by

$$D = a k^{-6} b^{6-3} (b^2 - 1), \quad (6)$$

$$x_0 = k^{-1/\beta} (b^2 - 1). \quad (7)$$

By analyzing the data in terms of two different equations, we have some check on possible bias that might be introduced by the use of a phenomenological equation. If we require that the two equations yield the same coefficients of the power laws for the critical isotherm and for the compressibility, we obtain a relationship between the parameters of the MSLG equation and those of the linear model:

$$E_2^{-1} = \frac{b^{2\beta(\delta-3)}/(\gamma-1)}{(b^2-1)^{2\beta}} - 1, \quad (8)$$

$$E_1 = \frac{a(b^2-1)^\gamma}{k^\delta E_2^{(\gamma-1)/2\beta}}. \quad (9)$$

For four of the gases studied, namely ⁴He, Xe, CO₂, and H₂O experimental P - V - T data¹⁵⁻¹⁸ were

converted earlier to chemical potential data.^{13,19} For ⁴He and CO₂ we found it necessary to make a few corrections in the chemical-potential data presented earlier; they are incorporated in tables of chemical-potential data which will be documented elsewhere.²⁰ For ³He we used the chemical-potential data²¹ that were deduced by Wallace and Meyer from their experimental P - V - T data.²² Those data were taken that refer to a range of temperatures and densities where the chemical potential μ is antisymmetric with respect to the critical density¹³ while data points perturbed by gravity effects were rejected. The data available for the analysis usually span a range of approximately $\pm 25\%$ in reduced density $\Delta\rho^*$, while the reduced temperature is in the range $10^{-4} < |\Delta T^*| < 3 \times 10^{-2}$. For the sixth fluid, O₂, we analyzed density-profile data that were determined by Weber²³ in the range $|\Delta\rho^*| < 0.2$ and $6 \times 10^{-5} < |\Delta T^*| < 2 \times 10^{-3}$.

A fit of the experimental $\Delta\mu^*$, $\Delta\rho^*$, ΔT^* data to each of these equations was achieved in the following steps. An error assignment was made to each triplet $\{\Delta\mu^*, \Delta\rho^*, \Delta T^*\}$ on the basis of the estimated experimental accuracy. Starting with a best estimate for T_c , coexisting liquid and vapor densities (ρ_L^* and ρ_G^*) were analyzed by a weighted fit in terms of²⁴

$$\frac{1}{2}(\rho_L^* - \rho_G^*) = B |\Delta T^*|^\beta, \quad (10)$$

yielding optimized values for β and $x_0 = B^{-1/\beta}$. For the six fluids studied it was verified that the exponent β was independent of the temperature range. The critical density ρ_c was determined either as the point of antisymmetry of the $\Delta\mu$ isotherms or from the diameter of the coexistence curve; it was checked whether both procedures yield the same values for ρ_c within the precision of the analysis.

As a next step the $\{\Delta\mu^*, \Delta\rho^*, \Delta T^*\}$ data were fitted by a weighted fit to each of the scaled equations, varying δ and T_c stepwise on a grid. In the case of the MSLG equation, the constants E_1 and E_2 followed from the fit. In the case of the linear model, b^2 was also varied stepwise and the constant a with its standard deviation was determined by the fit. For each point on the grid we obtained a value of the reduced variance χ^2 . The best fit was the one that minimized χ^2 . If weights have been properly assigned and if the functional form of the equation is adequate, the minimum value of χ^2 should be close to unity. It was checked whether the optimum value obtained for T_c is consistent with the value used in (10). The critical pressure P_c appears only as a normalization factor in $\Delta\mu^*$ and is, therefore, not important in the analysis. It was simply taken as the experimental

pressure corresponding to the density and temperature attributed to the critical point.

III. TEST OF UNIVERSALITY

From the results of our fits we have reached the following conclusions: (i) the two equations fit the experimental data equally well, generally within the experimental error; (ii) the two equations yield minimum values of χ^2 at the same position (δ, T_c) on the grid; (iii) the value of E_2 is small and roughly the same for the six gases, while the optimum linear-model fits generally occur for b^2 close to the restricted value proposed by Schofield, Litster, and Ho (SLH)²⁵:

$$b_{\text{SLH}}^2 = (\delta - 3)/(\delta - 1)(1 - 2\beta). \quad (11)$$

Thus, in addition to the critical exponents, two free constants, D and x_0 , are indeed sufficient to fit the experimental data for the six gases, which confirms the first part of the hypothesis of universality.

Having verified the basic equivalence of the two scaled equations, our further considerations are based on one of them, for which we choose the linear model. In order to test the universality of the critical exponents, it is necessary to know the accuracy of the exponent values deduced. This is done by expanding the linear-model equations to linear order in all adjustable parameters in the vicinity of the optimum parameter set; then, a linear least-squares problem results that permits calculation of the variance-covariance matrix of the parameter adjustments by standard means. The details of this procedure will be published elsewhere.²⁰

In Table I we report the linear-model parameters for the six gases. The error in a is the standard deviation of the fit, while the errors in all other parameters were obtained from the diagonal elements of the variance-covariance matrix. The

procedure for determining the errors in the parameters was developed specifically for the fit to the P - V - T data and was not applicable to the density profile data for oxygen.

It is seen that the exponents listed in Table I have the value $\beta = 0.355$ in common within one standard deviation and the value $\delta = 4.35$ within two standard deviations. The "universal" values $\beta = 0.355 \pm 0.007$ and $\delta = 4.35 \pm 0.10$ agree within combined error with all experimental values reported here. From the individual values of β and δ , the values of the exponents α and γ are obtained with the aid of the relations (2). The "universal" values

$$\begin{aligned} \alpha &= 0.10 \pm 0.04, \quad \beta = 0.355 \pm 0.007, \\ \gamma &= 1.19 \pm 0.03, \quad \delta = 4.35 \pm 0.10 \end{aligned} \quad (12)$$

span all the individual values as well as many values reported in the literature for these gases^{26,27} and other gases; for a review see, for instance, Ref. 8. We conclude that the hypothesis of universality is valid for these gases to within the current experimental accuracy.

IV. HYPERSCALING

In the critical region the correlation length becomes much larger than the range of the intermolecular forces. Hence, the detailed shape of the molecules is not expected to affect the mathematical character of the thermodynamic anomalies.²⁸ This leads, on the one hand, to the hypothesis of universality, and, on the other hand, to a connection between thermodynamic anomalies and the singular behavior of the correlation function. The latter is characterized by the exponents ν and η . A relationship between these exponents and the thermodynamic exponents is provided by the proposed hyperscaling relations^{9,10}

TABLE I. Linear-model parameters from statistical fit, $b^2 = b_{\text{SLH}}^2$.

	³ He	⁴ He	Xe	CO ₂	H ₂ O	O ₂
x_0	0.480 ± 0.02	0.369 ± 0.02	0.186 ± 0.1	0.142 ± 0.006	0.100 ± 0.01	0.184
a	4.16 ± 0.1	6.4 ± 0.1	17.7 ± 0.5	21.8 ± 0.4	24.5 ± 0.3	15.5 ± 0.7
b_{SLH}^2	1.364 ± 0.003	1.389 ± 0.006	1.407 ± 0.04	1.382 ± 0.006	1.429 ± 0.004	1.383
β	0.358 ± 0.005	0.356 ± 0.006	0.350 ± 0.04	0.349 ± 0.005	0.350 ± 0.013	0.353
δ	4.26 ± 0.04	4.34 ± 0.06	4.46 ± 0.3	4.44 ± 0.06	4.50 ± 0.13	4.37
$\alpha = 2 - \beta(\delta + 1)$	0.115	0.101	0.089	0.104	0.075	0.104
$\gamma = \beta(\delta - 1)$	1.168	1.188	1.211	1.199	1.225	1.190

$$d\nu = 2 - \alpha, \quad \frac{2 - \eta}{d} = \frac{\delta - 1}{\delta + 1}, \quad (13)$$

where d is the dimensionality of the system. These relations play a fundamental role in the renormalization theory of critical phenomena.^{3,4} They are satisfied for the two-dimensional Ising model and the three-dimensional spherical model for which the exponents are known exactly. However there exists some uncertainty about the validity of the hyperscaling relations for the three-dimensional Ising model.²⁹

We will now investigate the validity of the hyperscaling relations for gases. The experimental values for the exponent ν obtained from scattering data for such gases as argon and carbon dioxide center around $\nu = 0.63 \pm 0.02$.³⁰⁻³² From neutron scattering data an accurate value for the exponent η of neon, $\eta = 0.11 \pm 0.03$, was recently reported by Warkulwiz, Mozer, and Green³³; x-ray-scattering data of argon, recently obtained by Lin and Schmidt are in agreement with this value.³² Substitution of the thermodynamic exponents $\alpha = 0.10 \pm 0.04$ and $\delta = 4.35 \pm 0.10$ into (13) yields, on the other hand, $\nu = 0.63 \pm 0.015$ and $\eta = 0.12 \pm 0.02$, in remarkable agreement with the values determined experimen-

tally from scattering data; this supports the validity of the hyperscaling relations (13) for gases.

V. UNIVERSAL SCALED EQUATION OF STATE PARAMETERS

On the assumption that the hypothesis of universality is valid for gases, we have composed a table of critical-region parameters for a number of gases. For this purpose we accepted the values $\beta = 0.355$ and $\delta = 4.352$ and the corresponding values $E_2 = 0.289$ and $b^2 = b_{\text{SLH}}^2 = 1.3908$ in accordance with (8) and (11). From the coexistence-curve data we calculated the parameter x_0 corresponding to $\beta = 0.355$. For the six gases discussed above, we then determined the parameter E_1 by refitting the MLSG equation to the experimental chemical-potential data keeping the other parameters fixed. The corresponding linear-model parameter a then follows from (7) and (9). For the other gases the parameter a , and hence E_1 , was estimated from whatever information we could find on the shape of the critical isotherm or the compressibility along the critical isochore.²⁰ The results are presented in Table II. References to the sources consulted in preparing this table are also included.

TABLE II. Critical-region parameters for 14 fluids based on "universal" exponents.

	Critical-point parameters			Critical-region parameters		
	P_c (MPa)	ρ_c (kg/m ³)	T_c (K)	x_0	a	E_1
³ He ^a	0.116 78	41.45	3.3099	0.489	4.63	2.99
⁴ He ^b	0.227 42	69.6	5.1895	0.369	6.42	2.68
Ar ^c	4.865	535	150.725	0.183	16.5	2.34
Kr ^d	5.4931	908	209.286	0.183	16.5	2.34
Xe ^e	5.8400	1110	289.734	0.183	16.5	2.34
O ₂ ^f	5.043	436.2	154.580	0.183	15.6	2.21
N ₂ ^g	3.398	313.9	126.24	0.164	18.2	2.17
CH ₄ ^h	4.595	159.6	190.555	0.164	17.0	2.03
C ₂ H ₄ ⁱ	5.0390	215	282.344	0.166	17.5	2.13
<i>p</i> -H ₂ ^j	1.285	31.39	32.935	0.280	9.6	2.34
CO ₂ ^k	7.3753	467.8	304.127	0.141	21.8	2.06
NH ₃ ^l	11.303	235	405.4	0.109	21.4	1.37
H ₂ O ^m	22.06	322.2	647.13	0.100	22.3	1.24
D ₂ O ⁿ	21.66	357	643.89	0.100	22.3	1.24
	$\beta = 0.355$	$\delta = 4.352$		$b_{\text{SLH}}^2 = 1.3908$		
	$\gamma = 1.190$	$\alpha = 0.100$		$E = 0.287$		

^a References 21, 22.

^b References 15, 34.

^c Reference 35.

^d Reference 36.

^e Reference 16.

^f Reference 23.

^g References 37-40.

^h References 41, 42.

ⁱ References 43-46.

^j References 47, 48.

^k References 17, 44.

^l References 49-51.

^m References 18, 52.

ⁿ References 52, 53.

The critical temperatures are expressed in the currently accepted international practical temperature scale (IPTS-68) with the exception of those of ^3He and ^4He which are expressed in terms of the 1958 ^4He vapor-pressure scale.

Note added in proof. Our analysis shows that the critical exponents deduced from the density-profile data of O_2 are in good agreement with those deduced from the P - V - T data of other gases. Whether this is generally the case has been put into question as a consequence of recent density-profile experiments.⁵⁴

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*On leave of absence from the National Bureau of Standards, Washington, D. C. 20234.

†On sabbatical leave from the Institute for Molecular Physics, University of Maryland, College Park, Maryland 20742.

¹R. B. Griffiths, Phys. Rev. Lett. 24, 1479 (1970).

²D. D. Betts, A. J. Guttman, and G. S. Joyce, J. Phys. C 4, 1994 (1971).

³S. K. Ma, Rev. Mod. Phys. 45, 589 (1973).

⁴K. G. Wilson and J. Kogut, Phys. Rep. 12C, 75 (1974).

⁵S. Milošević and H. E. Stanley, Phys. Rev. B 5, 2526 (1972).

⁶F. L. Lederman, M. B. Salamon, and L. W. Shacklette, Phys. Rev. B 9, 2981 (1974).

⁷D. Stauffer, M. Ferer, and M. Wortis, Phys. Rev. Lett. 29, 345 (1972).

⁸J. M. H. Levelt Sengers, Physica (Utrecht) 73, 73 (1974).

⁹B. Widom, J. Chem. Phys. 43, 3898 (1965).

¹⁰G. Stell, Phys. Rev. Lett. 24, 1343 (1970).

¹¹R. B. Griffiths, Phys. Rev. 158, 176 (1967).

¹²D. S. Gaunt and C. Domb, J. Phys. C 3, 1442 (1970).

¹³M. Vicentini-Missoni, J. M. H. Levelt Sengers, and M. S. Green, J. Res. Natl. Bur. Stand. A 73, 563 (1969).

¹⁴P. Schofield, Phys. Rev. Lett. 22, 606 (1969).

¹⁵P. R. Roach, Phys. Rev. 170, 213 (1968).

¹⁶H. W. Habgood and W. G. Schneider, Can. J. Chem. 32, 98 (1954).

¹⁷A. Michels, B. Blaisse, and C. Michels, Proc. R. Soc. A 160, 358 (1937).

¹⁸S. L. Rivkin *et al.*, Teploenergetika 9(1), 57 (1962);

10(9), 66 (1963); 11(10), 72 (1964); 13(4), 59 (1966).

¹⁹J. M. H. Levelt Sengers and S. C. Greer, Int. J. Heat Mass Transfer 15, 1865 (1972).

²⁰J. M. H. Levelt Sengers, W. L. Greer, and J. V. Sengers, J. Phys. Chem. Ref. Data (to be published).

²¹B. Wallace and H. Meyer, "Tabulation of the Original Pressure-Volume-Temperature Data for He^3 - He^4 Mixtures and for He^3 ," technical report, Department of Physics, Duke University, Durham, N. C., 1971 (unpublished).

²²B. Wallace and H. Meyer, Phys. Rev. A 2, 1563 (1970); 2, 1610 (1970).

²³L. A. Weber, Phys. Rev. A 2, 2379 (1970).

²⁴J. M. H. Levelt Sengers, J. Straub, and M. Vicentini-Missoni, J. Chem. Phys. 54, 5034 (1971).

²⁵P. Schofield, J. D. Litster, and J. T. Ho, Phys. Rev.

Lett. 23, 1098 (1969).

²⁶H. A. Kierstead, Phys. Rev. A 7, 242 (1973).

²⁷J. Thoen and C. W. Garland, Phys. Rev. A 10, 1311 (1974)

²⁸L. P. Kadanoff, in *Critical Phenomena, Proceedings of the International School of Physics "Enrico Fermi," Course LI*, edited by M. S. Green (Academic, New York, 1971), p. 100.

²⁹A. Hankey and H. E. Stanley, Phys. Rev. B 6, 3515 (1972).

³⁰J. H. Lunacek and D. S. Cannell, Phys. Rev. Lett. 27, 841 (1971).

³¹B. Chu, Ber. Bunsenges. Phys. Chem. 76, 202 (1972).

³²J. S. Lin and P. W. Schmidt, Phys. Rev. A 10, 2290 (1974).

³³V. P. Warkulwiz, B. Mozer, and M. S. Green, Phys. Rev. Lett. 32, 1410 (1974).

³⁴M. R. Moldover, Phys. Rev. 182, 342 (1969).

³⁵S. Y. Wu, Ph.D. thesis (California Institute of Technology, Pasadena, 1972) (unpublished); C. J. Pings (private communication).

³⁶E. C. Gulari, Ph.D. thesis (California Institute of Technology, Pasadena, 1973) (unpublished); E. C. Gulari and C. J. Pings (private communication).

³⁷E. Mathias, H. Kamerlingh Onnes, and C. A. Crommelin, Communications Physical Laboratory, University of Leiden, No. 145C (1914).

³⁸H. Kamerlingh Onnes and Th. van Urk, Communications Physical Laboratory, University of Leiden, No. 169d (1924).

³⁹D. White, A. S. Friedman, and H. L. Johnston, J. Am. Chem. Soc. 73, 5713 (1951).

⁴⁰R. T. Jacobsen, Ph.D. thesis (Washington State University, Pullman, 1972) (unpublished).

⁴¹H. Gielen, V. Jansone, and O. B. Verbeke, J. Chem. Phys. 59, 5763 (1973).

⁴²J. D. Olson, J. Chem. Phys. (to be published).

⁴³E. Mathias, C. A. Crommelin, and H. Garfit Watts, Communications Physical Laboratory, University of Leiden, No. 189 (1927).

⁴⁴M. R. Moldover, J. Chem. Phys. 61, 1766 (1974).

⁴⁵J. R. Hastings and J. M. H. Levelt Sengers (unpublished results).

⁴⁶T. Wassenaar and N. J. Trappeniers (private communication).

⁴⁷R. D. Goodwin, D. E. Diller, H. M. Roder, and L. A. Weber, J. Res. Natl. Bur. Stand. A 67, 173 (1963).

⁴⁸H. M. Roder, L. A. Weber, and R. Goodwin, Monograph

U. S. Natl. Bur. Stand., No. 94 (1965).

⁴⁹K. Date, Rev. Phys. Chem. Jpn. 43, 17 (1973).

⁵⁰L. Haar, J. Phys. Chem. Ref. Data (to be published).

⁵¹T. A. Murphy (private communication).

⁵²G. Blank, Wärme und Stoffübertragung 2, 53 (1969).

⁵³J. Jůsa, R. Mareš, and O. Šifner, in Proceedings of the Eighth International Conference on the Properties of Steam (to be published).

⁵⁴R. J. Hocken (private communication).