Revised and extended scaling for coexisting densities of SF$_6$

Marcos Ley-Koo

Facultad de Ciencias, Universidad Nacional Autonoma de Mexico, Mexico 20, D. F.

Melville S. Green*

Department of Physics, Temple University, Philadelphia, Pennsylvania 19122
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The data of Weiner, Langley, and Ford on both the sum and difference of coexisting densities of SF$_6$ are found to be consistent, within a range of 2% in reduced temperature of T_c, with the series of terms (revised and extended scaling) predicted by renormalization group calculations. The hypothesis that the relatively small range of applicability of this series is due to a crossover to Van der Waals behavior is supported by further analysis.

Among the unexpected results predicted by recent theories of critical phenomena is the rectilinear behavior of the diameter of the coexistence curve as a function of temperature near the critical point. This was pointed out by Green, Cooper, and Sengers[1] (GCS) in a proposal to extend the range of ordinary scaling, and by Mermin[2] through examination of certain solvable models. Both predicted a leading behavior of the form

$$\tfrac{1}{2}(\rho_L + \rho_G) \simeq \rho_c + D\left|-t\right|^{1-\alpha}, \tag{1}$$

with $t = (T - T_c)/T_c$ and α the critical exponent describing the C_v singularity. Deviations from a rectilinear diameter have been reported for several binary mixtures.[3] For pure fluids, this effect has been observed by Weiner, Langley, and Ford[4] (WLF) in a recent experiment on SF$_6$.

As part of an investigation to find the consequences of the renormalization group for the thermodynamics of the critical point of fluids, we have derived expansions in nonintegral powers of t for a number of thermodynamic functions including the sum and difference of coexisting densities. Both the premises and results of these expansions agree in leading order with the revised scaling proposal of Mermin rather than that of GCS. The purpose of this comment is to report on our results from a least-squares analysis fit of our expressions to the experimental data of WLF on coexisting densities of SF$_6$. Our conclusion is that the experimental data can be well represented by the renormalization-group expressions with reasonable values of the exponents for $\left|-t\right| \le 2 \times 10^{-2}$ ($\left|\Delta T\right| < 7$ °K). We have also examined the hypothesis that the rather small range of applicability of the renormalization group (RG) is a manifestation of a crossover to mean-field behavior for $\left|t\right| > 10^{-2}$.

To obtain our expressions, we have made use of the general form for the thermodynamic potential proposed by Wegner.[5] For a fluid, this is

$$p = p v_c / k_B T = p_0(\tilde{\mu}, t) + p_s(g_E, g_H, g_1, g_2), \tag{2}$$

where $\mu = (\tilde{\mu} - \mu_c)/\mu_c$ is the reduced chemical potential difference and V_c the critical volume per molecule. The nonsingular part p_0 and the scaling fields g_E, g_H, g_1, g_2 may be expanded in integral powers of the physical variables $\tilde{\mu}, t$. The singular part p_s is a generalized homogeneous function which satisfies

$$p_s(g_E, g_H, g_1, g_2)$$
$$= \left|g_E\right|^{2-\alpha} p_s(\pm 1, g_H \left|g_E\right|^{-\Delta}, g_1 \left|g_E\right|^{\Delta_1}, g_2 \left|g_E\right|^{\Delta_2}), \tag{3}$$

where $+$ and $-$ are used to describe the one- and two-phase regions, respectively; p_s is a universal function which is dimensionless, as are the g's. The exponents Δ, Δ_1, and Δ_2 are positive quantities; g_E and g_H represent the two relevant scaling fields while g_K, $k = 1, 2$, represent the two most important irrelevant scaling fields. At the critical point, g_E and g_H will vanish, but g_1 and g_2 will in general have nonzero values. This means that the expansion of p_0, g_E, g_H, and g_K, $k = 1, 2$, in terms of $\tilde{\mu}$ and t will be of the form

$$p_0 = \tilde{p}_{00} + \tilde{p}_{10}\tilde{\mu} + p_{01}t + O(\tilde{\mu}^2, t^2), \tag{4}$$

$$g_h = \tilde{g}_{10}^h \tilde{\mu} + \tilde{g}_{01}^h t + O(\tilde{\mu}^2, t^2), \tag{5}$$

$$g_E = \tilde{g}_{10}^E \tilde{\mu} + \tilde{g}_{01}^E t + O(\tilde{\mu}^2, t^2), \tag{6}$$

$$g_k = \tilde{g}_{00}^k + \tilde{g}_{10}^k \tilde{\mu} + \tilde{g}_{01}^k t + O(\tilde{\mu}^2, t^2), \quad k = 1, 2. \tag{7}$$

The coefficients in the expansions of the scaling fields are system dependent.

Although we have made no commitment to the exponents of the Ising model in Eq. (3), we have committed ourselves to its symmetry, i.e.,

TABLE I. Fitted parameters for Eq. (9).

	Two terms	Three terms	Four terms
ρ_c	$0.730\,49 \pm 0.0014$	$0.730\,24 \pm 0.0011$	$0.730\,47 \pm 0.0016$
D_0	$1.148\,67 \pm 0.439$	$2.428\,22 \pm 1.604$	$2.373\,16 \pm 1.07$
$1 - \alpha$	$0.849\,5 \ \ \pm 0.056$	$0.822\,9 \ \ \pm 0.08$	$0.829 \ \ \pm 0.08$
D_1		$-5.220\,92 \pm 2.26$	$-6.215\,63 \pm 1.54$
D_2			$9.041\,2 \ \ \pm 4.04$
$1 - \alpha + \Delta_1$			$1.343\,9 \ \ \pm 0.11$
χ^2	1.51	1.35	2.48
t_{max}	8.0×10^{-4}	3.0×10^{-3}	1.9×10^{-2}

$$p_s(\pm 1, g_h |g_E|^{-\Delta}, g_1 |g_E|^{\Delta_1}, g_2 |g_E|^{\Delta_2})$$
$$= p_s(\pm 1, -g_h |g_E|^{-\Delta}, g_1 |g_E|^{\Delta_1}, -g_2 |g_E|^{\Delta_2}) \quad (8)$$

Thus, g_1 and g_2 are the leading symmetric and antisymmetric irrelevant scaling fields, respectively.

Under these conditions, the diameter of the coexistence curve is given by

$$\rho_d = \tfrac{1}{2}(\rho_L + \rho_G)$$
$$= \rho_c + D_0 |-t|^{1-\alpha} + D_1 |-t| + D_2 |-t|^{1-\alpha+\Delta_1} + \cdots . \quad (9)$$

The difference of coexisting densities will be

$$(\rho_L - \rho)/2\rho_c = B_0 |-t|^{\beta} + B_1 |-t|^{\beta+\Delta_1}$$
$$+ B_2 |-t|^{\beta+2\Delta_1} + B_3 |-t|^{\beta+1} + \cdots . \quad (10)$$

The isothermal compressibility along the coexistence curve is

$$\frac{(\rho^{\pm})^2 K_T}{kT_c/\mu_c^2 V_c} = \Gamma_0 |-t|^{-\gamma} + \Gamma_1 |-t|^{-\gamma+\Delta_1}$$
$$\pm \Gamma_2 |-t|^{-\gamma+(\Delta-1)} + \cdots , \quad (11)$$

where + (−) refers to the high- (low-) density branch. For the constant-volume specific heat along the critical isochore, we get

$$C_v/k_B = A_1 |-t|^{-\alpha} + A_0 + A_2 |-t|^{-\alpha+\Delta_1} + \cdots . \quad (12)$$

We have attempted to fit Eq. (9) to the data of Weiner,[6] corrected for the dependence of polarizability on density. In order to determine the range of validity of this equation, we have carried out the fitting as a function of range. This has been done by starting first with the asymptotic term and determining the largest interval $(0 \leq |-t| \leq t_{max})$ which gives a satisfactory fit. For a satisfactory fit we require, in addition to a minimum χ^2, that the parameters remain constant within their uncertainty as the temperature interval is increased up to t_{max}. We then proceed to add one more term in the expression and extend the range with an analogous requirement for a good fit. The best values for the various param-

eters are shown in Table I together with the terms needed in each temperature interval $0 \leq |-t| \leq t_{max}$.

Although for $|-t| > 0.01$ the diameter is approximately linear [see Fig. 1(b)] with a positive slope, we note that the coefficient of the linear term D_1 is negative; this is consistent with results obtained from analyses of specific-heat data, such as that by F. J. Cook[7] for ^{3}He, where the constant term in the specific heat is negative. Also, we note that our best value for the exponent, $1 - \alpha$, of the leading term in the diameter yields the value $\alpha = 0.15 \pm 0.06$, which may be compared to the value $\alpha = 0.14 \pm 0.07$ obtained by Edwards, Lipa, and Buckingham[8] for Xe from specific-heat measurements.

We have also attempted to fit the expression for the difference of coexisting densities, given by Eq. (10), to Weiner's[6] data. The results are indicated in Table II; t_{max} has the same significance as in the fits of the diameter. We note that our best value for β which we take to be its value for the three-term fit, $\beta = 0.327 \pm 0.003$, is considerably different from the value $\beta = 0.355$ suggested by Sengers and Sengers[9] as universal for fluids, but it is in agreement with the value obtained by Hocken and Moldover[10] for a temperature interval closer to the critical point than the present data. However, if we attempt to fit Eq. (10) over the whole range $0 \leq |-t| \leq 0.055$, an exponent $\beta = 0.34 \pm 0.001$ is obtained, but the deviations are systematic. Thus, the results of these fits together with the experiment of Hocken and Moldover[10] may be taken to mean that the true value of β is closer to, but somewhat higher than, the value 0.3125, given by high-temperature series expansion for the Ising model, than to the value 0.355 suggested by classical P-V-T measurements. The latter value is the result of attempting to fit over too wide a range with a single term and is not representative of the true universal value. We note also that the values of Δ_1, obtained from both the difference and the sum of coexisting densities, is $\Delta_1 = 0.49 \pm 0.04$, consistent with theoretical es-
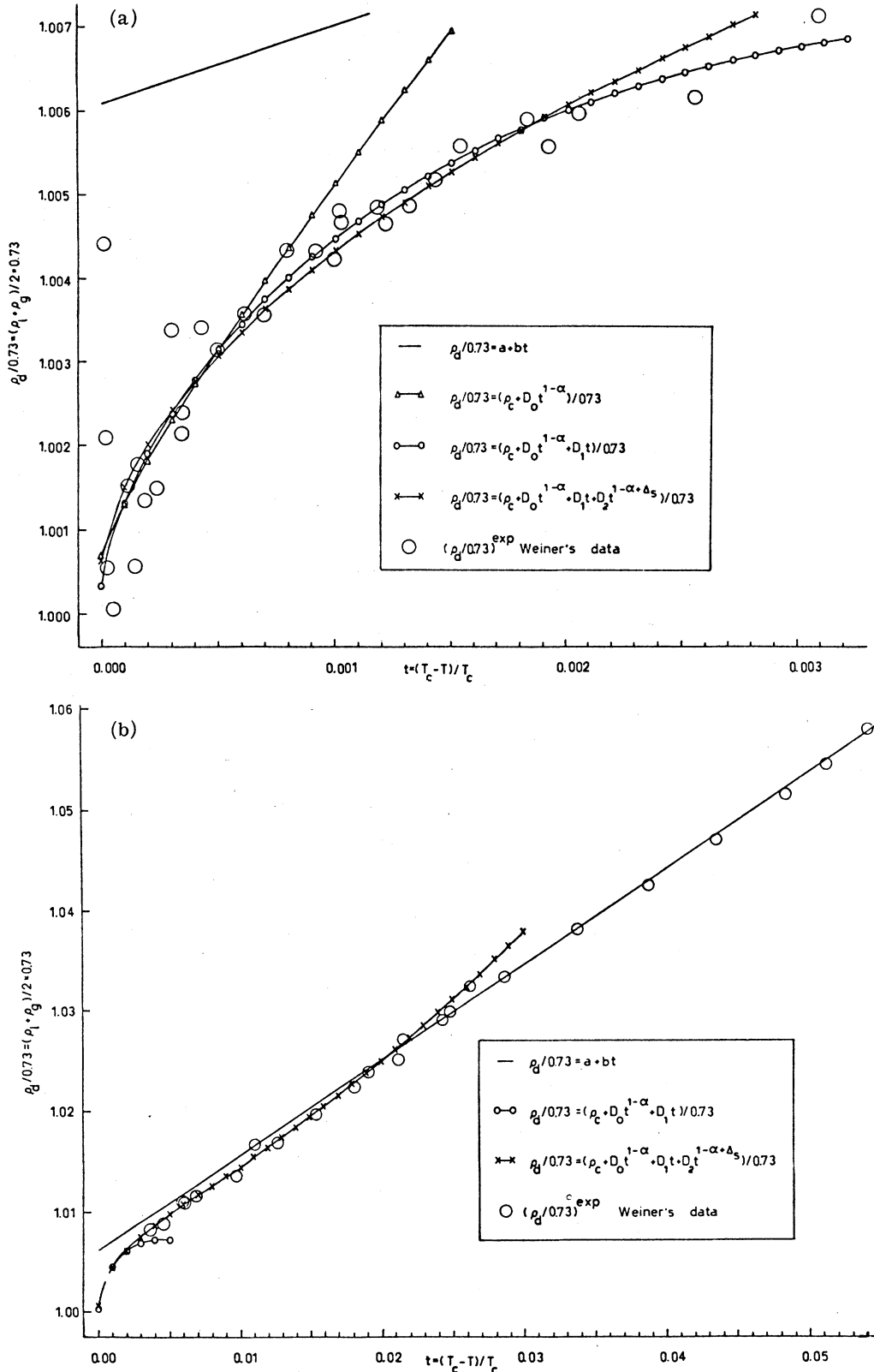
FIG. 1. Theoretical and experimental comparison of the diameter of SF_6 for temperature ranges of (a) $0 \leq |-t| \leq 0.0035$ and (b) $0 \leq |-t| \leq 0.055$.

TABLE II. Fitted parameters for Eq. (10).

	One term	Two terms	Three terms
B_0	$1.741\,34 \pm 0.604$	$1.722\,34 \pm 0.064$	1.7147 ± 0.016
β	$0.327\,7 \pm 0.082$	$0.327\,3 \pm 0.005$	$0.327\,1 \pm 0.001$
B_1		$0.742\,23 \pm 0.41$	$0.820\,3 \pm 0.043$
$\beta + \Delta_1$		$0.853\,2 \pm 0.21$	$0.821\,5 \pm 0.026$
B_2			$-1.439\,6 \pm 0.24$
$\beta + 2\Delta_1$			$1.298\,9 \pm 0.09$
T_c	318.703 ± 0.0005	318.703 ± 0.0002	318.703 ± 0.0001
χ^2	1.19	2.11	2.57
t_{max}	7.0×10^{-4}	1.0×10^{-2}	2.1×10^{-2}

timates.[11] Δ_2 is estimated to be ~1.5 and therefore is neglected.

One of the most obvious features of the diameter is that although a single term of the form $|-t|^{1-\alpha}$ gives a good representation of the data close to $T_c(|-t| < 10^{-3})$ (see Fig. 1a) it seems to be asymptotically linear away from the critical point ($|-t| > 10^{-2}$) [see Fig. 1(b)]. Since a rectilinear diameter is characteristic of the Van der Waals, or mean-field, equation of state and since the RG theory itself is supposed to represent the deviations from mean-field theory due to fluctuations, it is suggestive to suppose that the rather small range ($|-t| \sim 10^{-2}$) where Eqs. (9)–(10) are valid, is a reflection of the crossover to a Van der Waals or mean-field-like behavior. In order to test this idea we have first attempted to fit an equation of the form

$$\rho_d / \rho_c = (\rho_L + \rho_G)/2\rho_c = a + b(-t), \qquad (13)$$

to the data corresponding to the asymptotically rectilinear portion of the diameter, and we have obtained

$$a = 1.006\,09, \quad b = 0.948\,84$$

with $T_c = 318.703$ °K for $2 \times 10^{-2} < |-t| < 5.5 \times 10^{-2}$. The lower limit of the interval is the lowest temperature for which a and b remain constants, within uncertainties, and for which Eq. (13) gives a good description of the data.

The above assumption implies the existence of an "effective critical temperature" T_c^e such that the diameter is in fact a linear function of $-t^e = (T_c^e - T)/T_c^e$. We obtain T_c^e by extrapolation of the rectilinear portion to the critical density. This means that T_c^e will be given as the temperature for which $\rho_d = \rho_c$ if we assume that the "effective critical density," corresponding to the Van der Waals behavior, is the same as the true critical density; using the results from Eq. (13), we get

$$T_c^e = 320.75 \pm 0.06 \text{ °K} .$$

Thus, on this assumption the difference between

the Van der Waals critical temperature and the true critical temperature $T_c^e - T_c$ is 2.05 °K.

To further test the consistency of this picture, we have fitted an equation of the Van der Waals form to the density-difference data in the large t region. As in Eq. (13), we have used a two term expression,

$$(\rho_L - \rho_G)2\rho_c = b_{1/2}|-t^e|^{1/2} + b_{3/2}|-t^e|^{3/2}, \qquad (14)$$

where T_c^e is an adjustable parameter. The best values are

$$b_{1/2} = 3.264 \pm 0.06, \quad b_{3/2} = -6.692 \pm 0.351,$$

and $T_c^e = 320.77 \pm 0.01$ °K for 6 °K $< |\Delta T| < 17.5$ °K. It is gratifying to note that the two estimates for the effective Van der Waals critical temperature are the same within uncertainties. We note that Eq. (13) and (14) give a good description of the data in the range which begins at approximately the value of $|-t|$ for which Eqs. (9) and (10) cease to be applicable.

We draw the following conclusions: (i) The measured deviation from the rectilinear diameter is in agreement with the prediction of the renormalization group with an exponent α in agreement with the value obtained by direct measurements of C_v. (ii) The RG series represents both sum and difference of coexisting densities up to $t_{max} \sim 2 \times 10^{-2}$. (iii) The exponent β is close to, but somewhat higher than, the high-temperature series expansion value for the three-dimensional Ising model. (iv) The correction to scaling exponent is consistent with theoretical predictions of ~0.5.

Somewhat more tentatively we conclude that: (v) In a range which begins quite close to the critical point ($|t| > 2 \times 10^{-2}$) both the sum and difference of coexisting densities are represented by a Van der Waals or mean-field theory. (vi) The effective Van der Waals critical temperature is about 2 °K higher than the true critical temperature and the effective Van der Waals critical density is the same as the critical density.

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