

# Experimental and Theoretical Study of the Equation of State of CHF<sub>3</sub> in the Near-Critical Region

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The pressure-density-temperature ( $p$ - $\rho$ - $T$ ) surface of CHF<sub>3</sub> has been measured in the near-critical region by using an expansion-type apparatus. The data overlap with other previously published data for the classical region and seem compatible with results already reported for the critical region. The abilities of two revised and extended scaling equations of state for predicting the data have been tested. The equation of Sengers et al. describes the data satisfactorily, though in a quite limited region around the critical point. The results obtained with the equation of Anisimov et al. lead to similar results, though its applicability is restricted to a smaller region around the critical point. A classical equation with modified thermodynamic fields, leading to the correct scaling asymptotic behavior, describes the near-critical data as well as the equation of Sengers et al. while giving a better description of the crossover region.

## Introduction

The classical region of the liquid-vapor phase transition has been studied in the framework either of liquid-state theory<sup>1</sup> or of renormalization group (RG).<sup>2</sup> It has become clear that perturbative approaches and integral equations are unable to give a realistic description of the critical region. On the other hand, the usual momentum space RG techniques provide information only about the universal quantities characterizing the scaling behavior near the critical point (CP).

Some attempts have concentrated upon the idea of combining separate classical and nonclassical equations of state (EoS), each describing its appropriate part of the phase diagram.<sup>3</sup> The crossover between these two regions is then smoothly switched by a third "switching" function. An important problem associated with this method is that of choosing a switching function so that the resulting behavior, in particular that of the second-derivative properties, is free from irregularities on the boundary between classical and nonclassical regions.

The RG approach leads to expressions for the thermodynamic potential in terms of two scaling fields.<sup>4</sup> One of these fields is conjugate to the order parameter, and the other plays the role of the temperature. The relationship between these scaling fields and the thermodynamic field variables accessible to experiment is not universal and is not known from theory for any real fluid system. Even though lattice-hole<sup>5</sup> or parametric models<sup>6</sup> can help in dealing with this problem, they allow one to describe only a very restricted class of fluid properties (those that are strongly divergent), and even then the description is confined to a very small neighborhood of the critical point. Moreover, the above-mentioned models lead to a symmetric phase diagram, which is in disagreement with the situation found in real fluids. A way to extend the range of validity of this type of EoS's has been the use of effective critical exponents<sup>7</sup> that differ from the universal values predicted by RG or from series expansions of the three-dimensional Ising model.<sup>8</sup> Of course, this is a nonsatisfactory procedure, which can be improved by extending the asymptotic equation so as to include correction-to-scaling terms<sup>4,9</sup> and by incorporating scaling fields that are combinations of the two mentioned above. Such mixing of fields arises from the fact that the fluctuations of particles  $\Delta n$  and of energy  $\Delta E$  at constant density  $\rho = \rho_c$  for a liquid are not statistically independent, and in consequence  $\Delta n$  and  $\Delta E$  can be represented as linear combinations of the corresponding quantities for a symmetric system.<sup>10</sup> The field mixing arises in a natural way in the decorated lattice gas<sup>11</sup> and also in

lattice models that include triplet interactions.<sup>12</sup>

In the past few years, the  $p$ - $\rho$ - $T$  surfaces of several pure fluids (steam,<sup>13</sup> isobutane,<sup>14</sup> CO<sub>2</sub>,<sup>15</sup> and CH<sub>4</sub>,<sup>16</sup>) have been analyzed in terms of an extended and revised scaling EoS proposed by Sengers and Levelt Sengers.<sup>4</sup> Furthermore, steam has also been analyzed by using a similar EoS developed by Anisimov et al.<sup>17</sup> in terms of extended scaling and Prokovskii's transformation.<sup>10</sup> Even though these revised and extended scaling EoS's give very satisfactory results for describing thermodynamic variables in the near-critical region, they are applicable only to a small region around the CP, and they do not reduce to other well-known representations of fluid data away from the CP, such as the virial expansion.

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This can be explained in terms of which variables dominate the physical behavior in each of the regions of the phase diagram. In effect, very near the CP the correlation length  $\xi$  diverges, thus taking much larger values than the range of the intermolecular potential. These large-scale fluctuations dominate the physics of critical systems, allowing one to neglect any fluctuation whose range is smaller than a given cutoff length  $\Lambda$  in the momentum space RG technique.<sup>2,8,18</sup> Moreover, since  $\xi \rightarrow \infty$  at the CP, the value of  $\Lambda$  becomes unimportant, and any contributions to the thermodynamic properties of order  $1/(\Lambda\xi)^2$  are ignored (Wegner series<sup>4,19</sup>). According to this, it seems reasonable that such a theory cannot account for the transition from the CP to a region dominated by fluctuations of order  $\Lambda$ .

Recently, Albright and Nicoll<sup>20</sup> and Albright et al.<sup>21</sup> have presented preliminary results of a crossover theory that does not neglect the cutoff. When applied to the van der Waals equation, the theory allows one to describe both the classical and the critical regions of the phase diagram. On the other hand, important efforts have been made to derive a liquid-state theory with accurate critical-region behavior.<sup>22</sup> Parola and Reatto<sup>23</sup> have developed the so-called hierarchical reference theory of liquids, which together with an Ornstein-Zernike closure leads to a nonanalytical EoS in the critical region.<sup>24</sup> Nevertheless, the predicted critical exponents are not in agreement with those of the 3D Ising model.

These facts indicate that an accurate representation of the crossover between the scaling and the noncritical region is still an open problem in the theory of the fluid state. Moreover, for some of the fluids studied, the thermodynamic data were available in the two separate regions, but they were scarce in the crossover region, the data being obtained in different laboratories and with different samples. This can be an important problem since the coordinates of the critical point and the amplitudes of the scaling and correction-to-scaling terms are strongly sensitive to impurities,<sup>4,25,26</sup> and the values of  $T_c$ ,  $p_c$ , and  $\rho_c$  play an important role in the ability of the EoS to describe experimental data.<sup>3,14,15</sup>

Recently, some of us have reported an extensive study of the EoS of CHF<sub>3</sub> in the classical region:  $0.1 \leq p/\text{MPa} \leq 110$ ,  $126 \leq T/\text{K} \leq 332$ .<sup>27</sup> The data have been described by using an empirical multiparameter equation and show good agreement with other previous sets of data<sup>28</sup> and with values of second virial coefficients.<sup>29</sup> In addition, Narger et al.<sup>30</sup> have published a detailed study of the coexistence curve. Such data may allow one to determine some of the parameters that appear in the revised and extended scaling EoS.

The aim of the present paper is to present a detailed experimental study of the EoS of CHF<sub>3</sub> in the near critical region. The set of  $p$ - $\rho$ - $T$  data overlap with those presented in ref 27 for the classical region and approach the CP close enough as for extended scaling to be valid. The experiments will be performed on the same sample used for the classical region.<sup>27</sup> In this way, a very detailed  $p$ - $\rho$ - $T$  surface will be available for CHF<sub>3</sub> which, as already mentioned, is important for discussing present EoSs and

future developments on the crossover problem.

## Experimental Section

The data were obtained by the gas expansion technique, as described in detail by Calado et al.,<sup>31</sup> with a few minor modifications described elsewhere.<sup>32</sup> Further modifications were necessary for the near-critical region. To reduce gravity-induced density gradients, the cell was kept horizontal inside the water-glycol bath; in this way, the sample height was less than 25 mm. In addition the cell, the expansion line, and the zero element of the Ruska dead-weight gauge were kept at almost the same level. Also, due to the behavior of the transport coefficients near the CP,<sup>33</sup> long equilibration times (up to 4 h) were allowed after each expansion for those with  $|T - T_c| \leq 0.8$  K and  $|p - p_c| \leq 0.3$  MPa. A test similar to that described by Douslin et al.<sup>34</sup> was done for every point, discarding those for which there could be significant gravity-induced effects.

The temperature was controlled to within  $\pm 1$  mK and was measured with a platinum resistance thermometer. The temperature measurements have been referred to the IPTS-68 with an accuracy of  $\pm 0.02$  K. Pressures in the cell were measured with a Ruska dead-weight gauge, the accuracy being 0.1% or better and the precision being about 0.01%. Pressures in the expansion volumes were measured with a Texas Instruments quartz Bourdon gauge, with an accuracy of 0.015% and a precision of a few parts in 100 000. The main uncertainty in the  $p$ - $\rho$ - $T$  data arises from the calibration of the volumes of the system. From the combined errors in pressure, temperature, and volume, the estimated error is 0.1% for  $\rho \geq 8$  mol dm<sup>-3</sup>, 0.3% for  $2 \leq \rho$  mol dm<sup>-3</sup>  $\leq 8$ , and 0.4% below 2 mol dm<sup>-3</sup>. Most of our data correspond to  $\rho > 9$  mol dm<sup>-3</sup>.

The CHF<sub>3</sub> used in this work was donated by the Linde Division of the Union Carbide Corp. It was purified by fractionation in a low-temperature column with a reflux ratio of 19/20. The final purity is estimated to be better than 99.9%. As already mentioned, it was the same sample used for the classical region.<sup>27</sup>

## Results

The more than 800 experimental points are collected in Table I. Our isotherms extrapolate quite smoothly to the coexistence curve data of Hori et al.<sup>28</sup> No such direct comparison can be done with the data of Narger et al.,<sup>30</sup> since their interferometric technique allows one to calculate only the differences of densities of the phases in coexistence.

For the data to be useful for crossover studies, they must extrapolate smoothly to the classical region. To test this point, some isotherms have been measured up to 100 MPa. These data should be described by the Strohbridge equation previously proposed:<sup>27</sup>

$$p = RT\rho + (A_1RT + A_2 + A_3/T + A_4/T^2 + A_5/T^4)\rho^2 + (A_6RT + A_7)\rho^3 + A_8T\rho^4 + A_{15}\rho^6 + [(A_9/T^2 + A_{10}/T^3 + A_{11}/T^4)\rho^3 + (A_{12}/T^2 + A_{13}/T^3 + A_{14}/T^4)\rho^5] \exp(A_{16}\rho^2) \quad (1)$$

where the parameters  $A_i$  are given in Table II and are the same as in ref 27. We have included more digits than statistically significant in order to avoid roundoff errors. We have not found statistically significant differences between the high-pressure ( $p > 15$  MPa) data reported in this paper and the data reported in ref 27. Therefore, we can conclude that from the viewpoint of the experimental data there is a smooth crossover on the  $p$ - $\rho$ - $T$  surface of CHF<sub>3</sub>, and thus the data are valid for discussing the performance of the EoSs available in the literature.

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## Discussion

**Revised and Extended Scaling EoSs.** Ley-Koo and Green<sup>4</sup> applied the Wegner expansion<sup>19</sup> to study the critical behavior of fluids. Levelt Sengers et al.<sup>13-15</sup> have derived an EoS for fluids based on the use of revised scaling fields and Ley-Koo and Green's work. The fundamental equation is expressed in terms of the intensive variables, namely, the pressure  $p$ , the temperature  $T$ , and the chemical potential  $\mu$ , which are reduced through

$$\begin{aligned} \tilde{T} &= T/T_c & \Delta\tilde{T} &= (T - T_c)/T_c & \Delta\tilde{\mu} &= \mu - \mu_0(\tilde{T}) \\ \tilde{\mu} &= \mu T_c \rho_c / T_c \rho_c & \tilde{\mu}_0 &= \mu_0(\rho_c, T) & \tilde{p} &= p T_c / T p_c \end{aligned} \quad (2)$$

The EoS takes the form

$$p = p_0(T, \mu) + |u_T|^{2-\alpha} f_{\pm} \left( \frac{u_H}{|u_T|^{\beta\delta}} \right) + u_1 |u_T|^{2-\alpha} f_{\pm,1} \left( \frac{u_H}{|u_T|^{\beta\delta}} \right) \quad (3)$$

with

$$u_H = \Delta\tilde{\mu} = \tilde{\mu} - \tilde{\mu}_0(\tilde{T}) \quad u_T = \Delta\tilde{T} + c\Delta\tilde{\mu} \quad (4)$$

where  $\tilde{p}_0(\tilde{T}, \mu)$  and  $\tilde{\mu}_0(\tilde{T})$  are analytic functions represented by truncated Taylor expansions:

$$\tilde{p}_0(\tilde{T}, \mu) = 1 + \sum_{i=1}^3 \tilde{p}_i(\Delta\tilde{T})^i + \Delta\mu + p_{11}\Delta T\Delta\mu \quad (5)$$

$$\tilde{\mu}_0(\tilde{T}) = \tilde{\mu}_c + \sum_{j=1}^3 \tilde{\mu}_j(\Delta\tilde{T})^j \quad (6)$$

The scaled equation for the singular part  $\Delta\tilde{p}(\tilde{T}, \tilde{\mu})$  of the potential  $\tilde{p}$  is specified by the parametric equations corresponding to Schofield's linear model:

$$u_H = \Delta\tilde{\mu} = r^{\theta\delta} a \theta (1 - \theta^2) \quad (7)$$

$$u_T = r(1 - b^2 \theta^2) \quad (8)$$

$$\tilde{p} = \tilde{p}_0(\tilde{T}, \tilde{\mu}) + r^{1-\alpha} a [k_0 p_0(\theta) + r^{\Delta} k_1 p_1(\theta)] \quad (9)$$

with

$$p_i(\theta) = p_{0i} + p_{2i}\theta^2 + p_{4i}\theta^4 \quad (10)$$

Equations 7-10 define a transformation from the physical variables  $\Delta\tilde{\mu}$  and  $\Delta\tilde{T}$  to the parametric variables  $r$  and  $\theta$ , where  $r$  is a measure of the distance from the critical point and  $\theta$  determines the location on a contour of constant  $r$ , such that  $\theta = \pm 1$  corresponds to the two branches of the coexistence curve.

The critical exponents  $\beta$ ,  $\delta$ , and  $\Delta$  and the coefficients  $b$ ,  $p_{0i}$ ,  $p_{2i}$ , and  $p_{4i}$  are universal constants, whose values have been taken from Albright et al.<sup>15</sup> and are shown in Table III. The scaling field amplitudes  $a$ ,  $k_0$ ,  $k_1$ , and  $c$  and the pressure background coefficients  $p_{11}$ ,  $p_1$ ,  $p_2$ , and  $p_3$  depend on the fluid.

Since the performance of scaling EoSs depends upon the coordinates of the CP, it is important to have reliable values for those variables. Hori et al.<sup>28</sup> have reported a detailed study of the vapor-pressure curve and the densities of the coexistence curve near the CP. From their data they report  $T_c = 299.01$  K,  $p_c = 4.816$  MPa, and  $\rho_c = 7.556$  mol L<sup>-1</sup>. On the other hand, Narger et al.<sup>30</sup> reported  $p_c = 4.75$  MPa,  $\rho_c = 0.527$  g cm<sup>-3</sup>, and  $T_c$  ranging from 298.95 to 299.16 K. They suggest that the drift in  $T_c$  could be due to the presence of impurities. An experiment performed in our apparatus indicated that presence of two phases at  $T = 298.05$  K and  $p = 4.78$  MPa. Thus, we have chosen Hori's results for the regression of our data.

For the fluids studied so far,<sup>13-16</sup> Levelt Sengers's EoS has been found to be valid for the intervals

$$-1.005 \leq \tilde{T} \leq -0.94 \quad 0.6 \leq \tilde{p} \leq 1.3$$

We have found a similar range for the validity of this EoS. Table III shows the optimum values of the substance-dependent parameters, and Figure 1 shows the deviations between experimental and calculated results, together with the residuals of the Strobridge EoS, as a function of the reduced density. For the sake of sim-

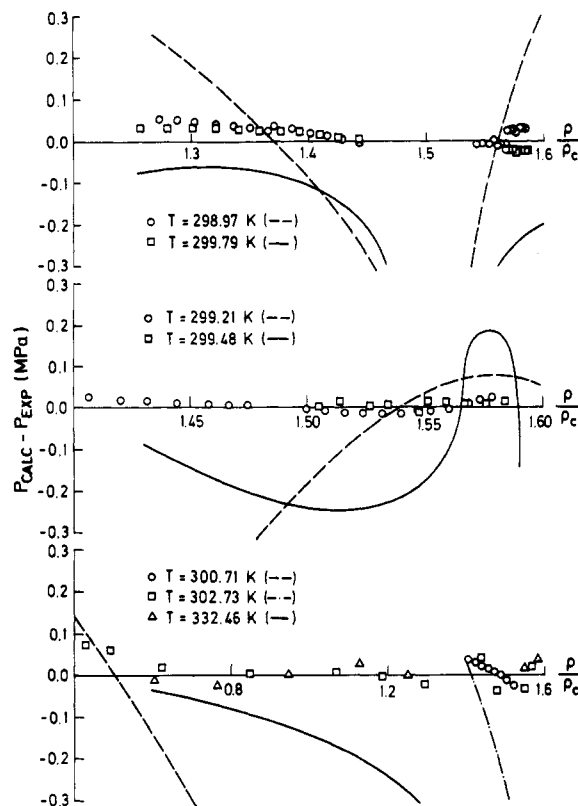


Figure 1. Differences between experimental and calculated pressures for several isotherms as a function of the reduced density. Symbols correspond to the extended and revised equation of state of Sengers et al., using the parameters of Table III. Lines correspond to the classical Strobridge equation of state, with the parameters of Table II (see text).

licity, these residuals have been represented by lines in Figure 1, since they have been calculated for a larger number of data points and they show a very smooth behavior. Even though the residuals are not randomly distributed, most of them are within the experimental uncertainty. Small changes in the critical point coordinates do not improve the results. The improvement with respect to the classical EoS is obvious near the CP, though one must emphasize that the residuals increase significantly outside the  $p$ ,  $\rho$ ,  $T$  region shown. This fact shows again the poor convergence properties of the Wegner expansion, and the need for the inclusion of medium-range fluctuations of the order of the cutoff parameter in the RG analysis. Similar conclusions were reached in the analysis of other fluids. Equations 3-10 provide expressions for the amplitudes of the leading terms of the extended scaling equations for different thermodynamic properties in terms of the universal and the fluid-dependent parameters mentioned above:

$$\tilde{p} - 1 = \pm B |\Delta\tilde{T}|^{\beta} \quad \text{for } \rho = \rho_c, T \leq T_c \quad (11)$$

$$\tilde{\chi} = \Gamma^+ |\Delta\tilde{T}|^{-\gamma} \quad \text{for } \rho = \rho_c, T \geq T_c \quad (12)$$

$$\Delta\tilde{\mu} = \pm D |\tilde{p} - 1|^{\delta} \quad \text{for } T = T_c \quad (13)$$

where  $B$ ,  $\Gamma^+$ , and  $D$  are defined through

$$B = k_0 / (b^2 - 1)^{\beta} \quad (14)$$

$$\Gamma^+ = k_0 / a_0 \quad (15)$$

$$D = a(b^2 - 1)b^{\delta-3} / k_0^{\delta} \quad (16)$$

subscript  $\sigma$  referring to the coexistence curve.

Using the critical amplitudes obtained by Narger et al.<sup>30</sup> and eqs 11-13, we have obtained  $a_0 = 22.7$  and  $k_0 = 0.22$ , which are in reasonable agreement with the values of Table III, especially considering the slight discrepancy in  $T_c$  and  $p_c$  referred to above. In any case, the discrepancy is similar to that obtained by Albright et al.<sup>15</sup> for CO<sub>2</sub>. Further test of the EoS cannot be done until

TABLE I: Experimental  $p$ - $\rho$ - $T$  Data for  $\text{CHF}_3$ 

$p/\text{MPa}$	$\rho/\text{mol dm}^{-3}$	$p/\text{MPa}$	$\rho/\text{mol dm}^{-3}$	$p/\text{MPa}$	$\rho/\text{mol dm}^{-3}$	$p/\text{MPa}$	$\rho/\text{mol dm}^{-3}$	$p/\text{MPa}$	$\rho/\text{mol dm}^{-3}$	$p/\text{MPa}$	$\rho/\text{mol dm}^{-3}$
$T = 285.13 \text{ K}$											
102.000	19.899	47.145	18.081	18.172	16.190	71.370	19.012	28.892	17.070	10.871	15.287
100.460	19.861	45.278	17.986	17.435	16.116	68.628	18.919	27.705	16.986	10.129	15.164
98.227	19.804	43.468	17.898	16.735	16.042	66.407	18.842	26.576	16.903	9.450	15.050
96.137	19.749	41.689	17.812	16.060	15.968	64.287	18.768	25.453	16.821	9.144	14.988
92.549	19.652	40.056	17.728	15.419	15.895	61.708	18.675	24.399	16.738	8.593	14.885
90.066	19.585	38.437	17.644	14.806	15.823	59.263	18.584	23.368	16.652	8.104	14.789
87.751	19.520	36.862	17.557	14.218	15.751	57.047	18.498	22.424	16.573	7.491	14.654
85.687	19.458	35.333	17.471	13.144	15.608	55.150	18.424	21.453	16.496	6.883	14.512
82.598	19.368	33.870	17.386	12.643	15.542	52.904	18.332	20.597	16.418	6.504	14.405
77.398	19.209	32.555	17.306	12.166	15.477	50.757	18.240	19.749	16.342	5.953	14.240
75.460	19.147	31.204	17.221	11.711	15.413	49.083	18.168	18.944	16.266	5.368	14.080
73.269	19.075	30.036	17.146	11.284	15.349						
$T = 293.10 \text{ K}$											
120.470	20.093	35.313	17.103	11.902	14.777	67.799	18.617	19.681	15.838	6.642	13.426
115.930	19.997	33.886	17.014	11.507	14.704	64.956	18.513	18.923	15.758	6.493	13.361
111.540	19.899	32.543	16.925	11.153	14.635	62.398	18.415	18.234	15.679	6.319	13.279
107.250	19.797	31.260	16.836	10.809	14.569	57.137	18.204	17.566	15.602	6.157	13.198
103.020	19.693	30.057	16.750	10.492	14.504	54.902	18.109	16.949	15.525	5.968	13.137
99.055	19.590	27.802	16.579	9.893	14.376	52.753	18.015	16.356	15.448	5.849	13.058
95.180	19.486	26.734	16.493	9.356	14.253	48.716	17.830	15.771	15.372	5.733	12.983
91.393	19.380	25.715	16.408	8.871	14.140	46.801	17.737	15.178	15.293	5.489	12.892
86.898	19.251	24.730	16.323	8.431	14.023	44.954	17.646	14.657	15.217	5.287	12.760
83.439	19.143	23.789	16.238	8.056	13.912	43.092	17.550	14.159	15.144	5.106	12.654
80.001	19.034	22.902	16.157	7.712	13.801	41.414	17.459	13.633	15.067	4.870	12.485
76.397	18.917	22.032	16.076	7.429	13.695	39.790	17.370	13.165	14.992	4.760	12.380
73.435	18.816	21.203	15.997	7.149	13.608	38.245	17.281	12.713	14.919		
70.537	18.716	20.431	15.917	6.826	13.495	36.718	17.191	12.297	14.846		
$T = 295.56 \text{ K}$											
25.446	16.257	12.090	14.596	7.296	13.349	17.283	15.426	9.027	13.886	6.201	12.830
24.881	16.211	11.739	14.524	7.193	13.310	16.707	15.349	8.821	13.830	6.139	12.772
23.960	16.133	11.408	14.451	7.089	13.276	16.122	15.273	8.635	13.774	5.891	12.650
23.106	16.055	11.084	14.383	6.993	13.208	15.591	15.196	8.442	13.721	5.772	12.561
22.252	15.977	10.781	14.316	6.896	13.178	15.068	15.120	8.270	13.668	5.726	12.516
21.432	15.897	10.499	14.250	6.828	13.144	14.572	15.046	8.104	13.618	5.567	12.461
20.679	15.818	10.210	14.186	6.745	13.120	14.129	14.961	7.953	13.568	5.450	12.352
19.938	15.739	9.957	14.122	6.676	13.094	13.681	14.886	7.801	13.522	5.280	12.179
19.239	15.661	9.702	14.061	6.610	13.071	13.261	14.813	7.663	13.476	5.071	11.985
18.558	15.583	9.440	14.004	6.547	13.033	12.847	14.740	7.533	13.431	4.964	11.855
17.910	15.504	9.243	13.943	6.277	12.887	12.462	14.668	7.409	13.389		
$T = 296.59 \text{ K}$											
103.730	19.605	54.131	17.934	20.776	15.729	74.041	18.715	35.195	16.926	10.185	14.087
102.370	19.570	52.036	17.837	17.201	15.311	71.274	18.615	33.898	16.838	9.427	13.901
98.476	19.467	50.027	17.744	16.074	15.154	68.509	18.516	31.411	16.665	8.788	13.719
94.670	19.361	48.110	17.651	15.020	15.001	65.905	18.417	29.120	16.493	8.242	13.544
89.819	19.221	44.461	17.466	14.067	14.850	63.434	18.331	28.036	16.406	6.986	13.057
86.519	19.122	42.759	17.374	13.221	14.706	60.979	18.224	26.011	16.235	5.560	12.187
83.205	19.019	39.547	17.193	12.421	14.556	58.577	18.126	24.078	16.055	5.120	11.775
80.036	18.917	38.024	17.103	11.718	14.429	56.317	18.030	22.358	15.891	4.851	11.383
76.986	18.815	36.587	17.014	11.043	14.289						
$T = 296.95 \text{ K}$											
18.213	15.442	9.287	13.829	6.469	12.742	12.413	14.544	7.186	13.082	5.790	12.274
17.600	15.363	9.082	13.770	6.377	12.722	12.048	14.475	7.089	13.043	5.742	12.232
17.023	15.285	8.882	13.711	6.301	12.673	11.697	14.407	7.001	13.005	5.698	12.188
16.466	15.207	8.510	13.601	6.230	12.622	11.373	14.339	6.917	12.969	5.652	12.182
15.931	15.131	8.194	13.493	6.163	12.582	11.077	14.271	6.839	12.935	5.608	12.140
15.414	15.055	8.035	13.442	6.104	12.536	10.781	14.206	6.765	12.903	5.567	12.098
14.916	14.981	7.886	13.391	6.049	12.490	10.498	14.141	6.697	12.877	5.526	12.065
14.448	14.907	7.760	13.340	5.994	12.446	10.223	14.078	6.641	12.837	5.487	12.041
13.991	14.834	7.505	13.247	5.939	12.404	9.978	14.014	6.580	12.800	5.447	12.005
13.563	14.761	7.392	13.203	5.891	12.358	9.509	13.889	6.522	12.769		
13.164	14.688	7.287	13.124	5.840	12.315						
$T = 298.76 \text{ K}$											
5.106	10.943	7.485	12.949	9.537	13.708	6.270	12.303	8.566	13.392	11.071	14.108
5.149	11.045	7.705	13.052	9.771	13.773	6.318	12.335	8.743	13.454	11.374	14.178
5.616	11.711	7.843	13.105	10.012	13.839	6.373	12.365	8.929	13.517	11.686	14.248
5.699	11.805	8.097	13.211	10.251	13.905	6.552	12.474	9.117	13.580	12.021	14.320
5.774	11.889	8.242	13.270	10.508	13.972	7.076	12.763	9.323	13.644		
5.843	11.958	8.442	13.327	10.781	14.042						
$T = 298.97 \text{ K}$											
4.903	9.619	5.994	11.978	8.311	13.264	4.919	9.849	6.045	12.019	8.637	13.384
4.911	9.734	6.017	12.000	8.469	13.324	4.931	9.979	6.067	12.043	8.816	13.445

TABLE I (Continued)

$p/\text{MPa}$	$\rho/\text{mol dm}^{-3}$	$p/\text{MPa}$	$\rho/\text{mol dm}^{-3}$	$p/\text{MPa}$	$\rho/\text{mol dm}^{-3}$	$p/\text{MPa}$	$\rho/\text{mol dm}^{-3}$	$p/\text{MPa}$	$\rho/\text{mol dm}^{-3}$	$p/\text{MPa}$	$\rho/\text{mol dm}^{-3}$
4.946	10.093	6.092	12.067	8.998	13.507	5.727	11.756	6.602	12.442	12.434	14.378
4.963	10.205	6.118	12.092	9.188	13.571	5.751	11.771	6.665	12.479	12.806	14.449
4.979	10.316	6.146	12.117	9.397	13.635	5.764	11.796	6.731	12.517	13.171	14.522
5.000	10.357	6.177	12.142	9.613	13.700	5.786	11.813	7.112	12.736	13.571	14.596
5.023	10.475	6.203	12.174	9.836	13.766	5.806	11.833	7.293	12.828	13.984	14.671
5.049	10.591	6.239	12.200	10.074	13.832	5.824	11.854	7.396	12.879	14.421	14.747
5.080	10.696	6.276	12.229	10.322	13.898	5.863	11.859	7.510	12.930	14.877	14.824
5.112	10.797	6.311	12.262	10.584	13.963	5.884	11.879	7.625	12.984	15.355	14.902
5.147	10.903	6.354	12.295	10.857	14.043	5.905	11.898	7.749	13.039	19.322	15.445
5.183	10.997	6.398	12.302	11.139	14.102	5.922	11.922	7.886	13.094	20.714	15.604
5.638	11.659	6.442	12.336	11.442	14.169	5.950	11.935	8.014	13.150		
5.674	11.698	6.495	12.369	11.759	14.238	5.971	11.957	8.157	13.207		
5.709	11.736	6.547	12.406	12.090	14.308						
$T = 299.21 \text{ K}$											
19.336	15.429	7.799	13.027	6.180	12.107	9.892	13.758	6.644	12.443	5.566	11.513
18.694	15.349	7.679	12.972	6.152	12.081	9.670	13.692	6.588	12.403	5.520	11.452
18.085	15.269	7.565	12.917	6.097	12.039	9.450	13.627	6.538	12.362	5.477	11.390
17.490	15.190	7.457	12.864	6.044	12.000	9.247	13.563	6.488	12.324	5.439	11.330
16.934	15.112	7.348	12.829	5.994	11.926	9.054	13.499	6.439	12.289	5.329	11.141
16.397	15.035	7.158	12.727	5.946	11.887	8.868	13.437	6.398	12.253	5.294	11.078
15.881	14.959	7.071	12.678	5.899	11.854	8.692	13.376	6.357	12.220	5.262	11.014
15.385	14.884	6.988	12.629	5.819	11.787	8.524	13.316	6.318	12.221	5.214	10.912
14.912	14.810	6.912	12.583	5.760	11.730	8.369	13.255	6.281	12.191	5.177	10.818
13.619	14.569	6.836	12.538	5.723	11.689	8.209	13.197	6.246	12.160	5.145	10.732
10.375	13.893	6.773	12.492	5.666	11.633	8.066	13.139	6.213	12.133	5.112	10.629
10.129	13.825	6.705	12.451	5.614	11.572	7.929	13.092				
$T = 299.48 \text{ K}$											
103.570	19.505	14.786	14.762	7.719	12.949	21.299	15.625	10.540	13.891	6.105	11.969
99.922	19.416	14.335	14.687	7.560	12.879	20.564	15.544	10.247	13.827	6.026	11.905
96.392	19.325	13.908	14.612	7.344	12.775	19.867	15.463	9.799	13.696	5.960	11.842
94.035	19.261	13.498	14.537	7.223	12.716	19.198	15.381	9.578	13.630	5.899	11.780
91.061	19.177	13.103	14.463	7.126	12.665	18.572	15.302	9.365	13.564	5.844	11.719
52.229	17.731	12.730	14.388	6.959	12.567	17.965	15.223	9.158	13.500	5.789	11.691
26.369	16.124	12.372	14.314	6.802	12.477	17.366	15.146	8.959	13.436	5.718	11.592
25.432	16.040	12.028	14.241	6.669	12.390	16.811	15.068	8.607	13.309	5.665	11.533
24.530	15.955	11.746	14.167	6.552	12.308	16.266	14.991	8.435	13.243	5.602	11.439
23.671	15.872	11.387	14.098	6.394	12.206	15.757	14.914	8.125	13.122	5.538	11.371
22.845	15.789	11.091	14.028	6.304	12.144	15.254	14.839	7.980	13.062		
22.053	15.708	10.809	13.959	6.201	12.052						
$T = 299.79 \text{ K}$											
10.285	13.774	7.147	12.633	6.175	11.989	8.206	13.104	6.478	12.219	5.191	10.521
10.047	13.710	7.067	12.574	6.146	11.964	8.054	13.048	6.432	12.185	5.153	10.398
9.799	13.646	6.982	12.530	6.118	11.939	7.925	12.992	6.391	12.153	5.117	10.259
9.620	13.587	6.908	12.484	6.089	11.917	7.792	12.938	6.348	12.123	5.090	10.126
9.417	13.525	6.836	12.441	6.067	11.890	7.675	12.884	6.310	12.093	5.065	9.983
9.213	13.462	6.767	12.399	6.040	11.868	7.560	12.831	6.274	12.065	5.041	9.834
8.841	13.340	6.698	12.361	6.017	11.845	7.453	12.778	6.240	12.037	5.019	9.673
8.674	13.279	6.635	12.325	5.930	10.902	7.347	12.728	6.205	12.015	5.000	9.496
8.499	13.221	6.580	12.288	5.273	10.768	7.245	12.680				
8.355	13.162	6.526	12.253	5.232	10.650						
$T = 300.34 \text{ K}$											
17.111	15.082	9.344	13.456	7.416	12.684	10.740	13.856	8.150	13.022	6.687	12.265
16.703	15.009	9.147	13.392	7.314	12.628	10.471	13.787	8.009	12.964	6.571	12.183
16.308	14.937	8.961	13.329	7.214	12.577	10.225	13.720	7.875	12.906	6.479	12.116
15.833	14.848	8.782	13.266	7.124	12.527	9.994	13.653	7.756	12.849	6.389	12.045
15.470	14.778	8.614	13.204	7.034	12.479	9.767	13.587	7.636	12.792	6.318	11.979
15.006	14.687	8.454	13.143	6.952	12.433	9.551	13.521	7.526	12.737	6.242	11.925
11.004	13.926	8.306	13.081	6.814	12.347						
$T = 300.71 \text{ K}$											
11.560	14.030	8.474	13.093	6.924	12.344	9.764	13.543	7.560	12.691	5.804	11.353
11.264	13.958	8.323	13.032	6.851	12.299	9.545	13.477	7.454	12.638	5.730	11.236
10.981	13.887	8.183	12.973	6.784	12.253	9.347	13.412	7.351	12.587	5.659	11.121
10.710	13.816	8.040	12.915	6.719	12.207	9.158	13.346	7.257	12.530	5.591	10.999
10.459	13.747	7.913	12.857	6.617	12.129	9.016	13.278	7.167	12.482	5.537	10.890
10.215	13.678	7.790	12.800	6.514	12.048	8.798	13.218	7.080	12.436	5.479	10.756
9.985	13.610	7.672	12.745	5.902	11.489	8.635	13.155	7.000	12.390	5.420	10.609
$T = 302.73 \text{ K}$											
54.475	17.697	30.063	16.256	6.819	11.832	40.325	16.948	23.472	15.658	4.085	2.676
50.523	17.509	29.003	16.170	6.605	11.693	38.858	16.859	21.942	15.489	3.974	2.538
48.661	17.415	27.981	16.085	5.966	10.849	37.434	16.771	20.510	15.308	3.855	2.399
45.133	17.228	27.003	16.000	4.996	4.710	36.091	16.684	8.883	12.968	3.629	2.158
43.469	17.135	26.066	15.914	4.458	3.231	34.768	16.598	8.419	12.779	3.380	1.917
41.868	17.036	24.303	15.744	4.238	2.884	33.519	16.512	8.146	12.657		

TABLE I (Continued)

$p/\text{MPa}$	$\rho/\text{mol dm}^{-3}$	$p/\text{MPa}$	$\rho/\text{mol dm}^{-3}$	$p/\text{MPa}$	$\rho/\text{mol dm}^{-3}$	$p/\text{MPa}$	$\rho/\text{mol dm}^{-3}$	$p/\text{MPa}$	$\rho/\text{mol dm}^{-3}$	$p/\text{MPa}$	$\rho/\text{mol dm}^{-3}$
$T = 306.17 \text{ K}$											
12.379	13.661	3.763	2.207	2.897	1.486	10.657	13.183	3.001	1.561		
$T = 313.21 \text{ K}$											
5.974	5.302	4.603	2.833								
$T = 322.90 \text{ K}$											
108.070	18.960	62.122	17.317	28.493	15.005	81.758	18.124	42.291	16.195	14.218	12.521
104.280	18.855	60.055	17.213	26.920	14.828	79.115	18.020	40.973	16.102	12.593	11.939
100.730	18.749	56.172	17.023	25.455	14.653	76.336	17.918	39.678	16.008	11.374	11.370
97.261	18.644	54.310	16.926	24.110	14.479	73.697	17.817	38.438	15.913	10.191	10.627
93.898	18.539	51.329	16.762	22.868	14.305	71.191	17.716	36.132	15.729	9.436	9.971
90.717	18.435	48.130	16.572	17.160	13.290	68.819	17.615	34.001	15.544	3.494	1.675
87.628	18.331	46.553	16.478	16.104	13.043	66.476	17.515	32.017	15.363	2.801	1.263
84.613	18.227	45.065	16.383	15.171	12.799	64.274	17.416	30.201	15.183	2.092	0.892
$T = 332.46 \text{ K}$											
106.950	18.647	50.633	16.316	18.957	12.896	74.399	17.508	40.793	15.634	9.847	8.518
101.900	18.498	49.083	16.219	17.127	12.438	70.805	17.354	36.642	15.286	8.821	7.160
98.571	18.392	47.241	16.098	15.474	11.944	68.529	17.252	35.062	15.141	7.898	5.784
95.324	18.287	44.736	15.928	14.786	11.702	53.923	16.510	33.457	14.987	7.028	4.570
77.860	17.664	42.931	15.797	10.719	9.434	52.256	16.413	31.997	14.836		

TABLE II:  $A_j$  Coefficients of the Strohbridge Equation of State for  $\text{CHF}_3$ 

$j$	$A_j$
1	$0.045457 \pm 0.003 \text{ dm}^3 \text{ mol}^{-1}$
2	$6.9009 \pm 0.07 \text{ bar dm}^6 \text{ mol}^{-2}$
3	$-5684.3 \pm 2 \text{ bar dm}^6 \text{ K mol}^{-2}$
4	$(5.8935 \pm 0.01) \times 10^5 \text{ bar dm}^6 \text{ K}^2 \text{ mol}^{-2}$
5	$-(2.6234 \pm 0.009) \times 10^9 \text{ bar dm}^6 \text{ K}^4 \text{ mol}^{-2}$
6	$-(6.9026 \pm 0.5) \times 10^{-3} \text{ dm}^{-6} \text{ mol}^{-2}$
7	$0.21356 \pm 0.007 \text{ bar dm}^9 \text{ mol}^{-3}$
8	$(2.2642 \pm 0.1) \times 10^{-5} \text{ bar dm}^{12} \text{ K}^{-1} \text{ mol}^{-4}$
9	$-33930 \pm 80 \text{ bar dm}^9 \text{ K}^2 \text{ mol}^{-3}$
10	$(2.9711 \pm 0.004) \times 10^7 \text{ bar dm}^9 \text{ K}^3 \text{ mol}^{-3}$
11	$-(3.4292 \pm 0.009) \times 10^9 \text{ bar dm}^9 \text{ K}^4 \text{ mol}^{-3}$
12	$47.361 \pm 0.3 \text{ bar dm}^{15} \text{ K}^2 \text{ mol}^{-15}$
13	$-64699 \pm 2 \text{ bar dm}^{15} \text{ K}^3 \text{ mol}^{-5}$
14	$(7.8646 \pm 0.008) \times 10^6 \text{ bar dm}^{15} \text{ K}^4 \text{ mol}^{-5}$
15	$(2.0224 \pm 0.007) \times 10^{-5} \text{ bar dm}^{18} \text{ mol}^{-6}$
16	$-0.0040000 \pm 0.001 \text{ dm}^6 \text{ mol}^{-2}$

TABLE III: Universal Constants and Parameters in the Equation of State of Sengers et al.

Universal Constants			
$P_{00} = 0.586535$	$P_{20} = -1.026243$	$P_{40} = 0.612903$	
$P_{01} = 0.103246$	$P_{21} = 0.160322$	$P_{41} = -0.169860$	
$b = 1.17290$	$\alpha = 0.1085$	$\Delta = 0.500$	
$\beta = 0.325$	$\delta = 4.820$		
Substance-Dependent Parameters			
$a = 23.046$	$k_0 = 1.2428$	$k_1 = 0.31114$	$c = -0.012471$
$\bar{p}_{11} = -0.07871$	$\bar{p}_1 = 6.3382$	$\bar{p}_2 = -21.669$	$\bar{p}_3 = 0.000$

derivatives of the  $p$ - $\rho$ - $T$  surface (speed of sound and heat capacity) are available.

Anisimov et al.<sup>17</sup> have reported an EoS based on extended scaling theory and Prokovskii's transformation.<sup>10</sup> They express the potential as

$$p = p_c \left[ \frac{\rho}{\rho_c} \Delta\mu(r, \theta) - \Psi(r, \theta) - \varphi(\Delta\tilde{T}) \right] \quad (17)$$

$$\varphi(\Delta\tilde{T}) = -1 + f_1 \Delta\tilde{T} + f_2 \Delta\tilde{T}^2 + f_3 \Delta\tilde{T}^3 + f_4 \Delta\tilde{T}^4 \quad (18)$$

where the  $f_i$ 's are substance-dependent parameters, and the parametric variables  $r$  and  $\theta$  are obtained through the transformation

$$\Delta\tilde{T} = r(1 - b^2\theta^2) \quad (19)$$

$$\Delta\rho = kr^{\beta}\theta + B_3\Delta\tilde{T} \quad (20)$$

with  $k$  and  $B_3$  being also substance-dependent.

TABLE IV: Substance-Dependent Parameters in Anisimov et al.'s Equation of State

$a = 22.007$	$d = 13.650$	$f = -71.732$
$c = 3.4640$	$k = 1.3298$	$f_1 = -7.8339$
$f_2 = 57.171$	$f_3 = -519.32$	$f_4 = 2559.1$

The chemical potential term is defined through

$$\Delta\mu(r, \theta) = \Delta\mu_{RG}(r, \theta) + r^{\Delta_A+1} [b_1 + (b_2 - b_1 b^2)\theta^2 + (b_3 - b_2 b^2)\theta^4] \quad (21)$$

where  $\Delta_A$  and the  $b_i$ 's are functions of the critical exponents, and

$$\Delta\mu_{RG}(r, \theta) = ar^{\beta}\theta(1 - \theta^2) + cr^{\beta\delta+\Delta}\theta \quad (22)$$

On the other hand

$$\Psi(r, \theta) = \Psi_{RG}(r, \theta) + kr^{2\gamma+3\beta-1}\theta[d + \frac{1}{3}[f - 2d(e - \beta)]b^2\theta^2 + (1 - 2\beta)/(5 - 2e)[de_1 + fe_2]b^4\theta^4] \quad (23)$$

where  $a$ ,  $c$ ,  $d$ , and  $f$  are new nonuniversal constants, and the  $e_i$ 's are again combinations of the critical exponents.

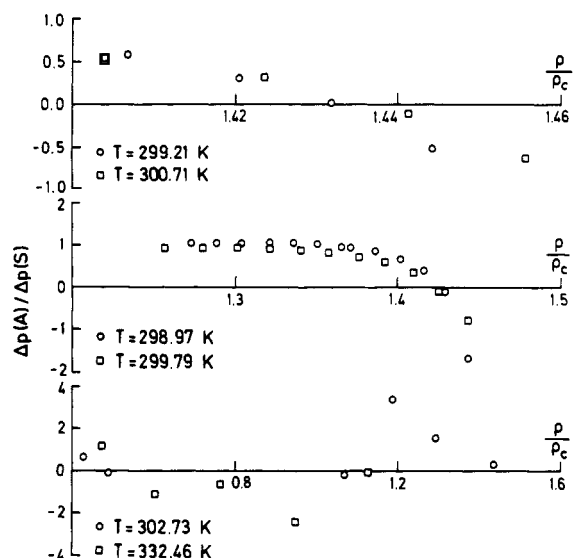
Finally

$$\Psi_{RG}(r, \theta) = \frac{ak}{2b^4} r^{2-\alpha} \left[ \frac{2\beta(b^2 - 1)}{2 - \alpha} + \frac{2\beta(2\gamma - 1)}{\gamma(1 - \alpha)} (1 - b^2\theta^2) + \frac{2\beta - 1}{\alpha} (1 - b^2\theta^2) \right] - \frac{kc}{2b^2} \frac{r^{2-\alpha+\Delta}}{1 - \alpha + \Delta} \left[ (1 - 2\beta)b^2\theta^2 - \frac{\gamma + \Delta}{2 - \alpha + \Delta} \right] \quad (24)$$

Table IV collects the values of the substance dependent parameters for the EoS of Anisimov et al.

As in the case of Sengers's EoS, some parameters can be traced back to the amplitudes of the leading scaling terms of thermodynamic properties. The results of N  rger et al.<sup>30</sup> lead to  $k = 1.2545$  and  $c/a = 0.5849$ . While this value of  $k$  does not differ significantly from the value of Table IV, the ratio  $c/a$  is quite different ( $c/a = 0.1574$  from Table IV). In addition, the diameter of the coexistence curve data<sup>30</sup> leads to  $B_3 = 1.40$ ; however, we have found no statistical differences between the results with  $B_3 = 0$  and  $B_3 = 1.40$ ; probably, the lack of data in the very near proximity of the CP makes  $B_3$  not significant. Finally, it must be emphasized that there is a strong correlation between the  $f_i$  parameters, the statistical significance of  $f_3$  and  $f_4$  being quite small.

Figure 2 shows the ratio of the residuals of the EoS's of Levett Sengers et al. and of Anisimov et al. for several near critical isotherms in the proximity of the CP, as a function of the reduced density. The results show that the performance of both equations



**Figure 2.** Ratio of the residuals of the equations of state of Anisimov et al. and of Sengers et al. as a function of the reduced density for several isotherms.

is quite similar to the near-critical region; though the residuals of Anisimov's EoS are slightly smaller than those of Levelt Sengers's EoS, serious problems of convergence in the fitting procedure limits the applicability of Anisimov's EoS to a more restricted region around the CP.

**Modified Classical EoS's.** Fox<sup>3</sup> showed that the description of thermodynamic properties can be significantly improved in the critical region by transforming an analytical EoS into a non-analytical EoS in a manner that preserves the classical behavior far from the CP but obeys scaling laws near the CP. This transformation is based on a state function  $\Psi$ , which measures the distance from the CP and is defined as

$$\Psi = p - p_c - \rho_c(\bar{\mu} - \bar{\mu}_c) - \bar{z}_c(T - T_c) \quad (25)$$

where

$$\bar{\mu} = (\mu - \mu^*) + RT \ln(\rho v_0) \quad (26)$$

$v_0$  being the unit volume, the asterisk referring to the ideal gas behavior, and

$$\bar{z} = \rho\{(s - s^*) + R[1 - \ln(v_0\rho)]\} \quad (27)$$

$s$  being the molar entropy.

The nonclassical EoS can be defined in terms of the following set of parametric equations:

$$T' = T_c + (T - T_c)g^\theta \quad (28)$$

$$\bar{\mu} = \bar{\mu}_c(T') + [\bar{\mu}(\rho, T) - \bar{\mu}_c(T)]g^\phi \quad (29)$$

$$p' = p + \rho_c(\bar{\mu}' - \bar{\mu}) + \bar{z}_c(T' - T_c) + Q[(T' - T_c)^2 - (T - T_c)^2] \quad (30)$$

where

$$\theta = 2\alpha/(2 - \alpha) \quad (31)$$

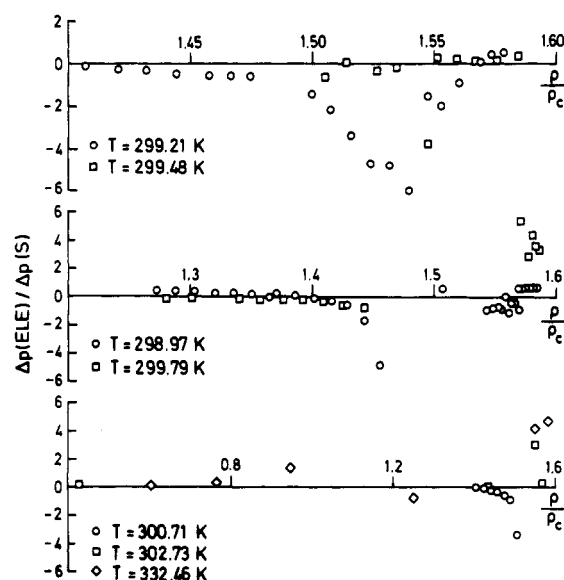
$$\phi = 1 - 2\beta[1 + \alpha/(2 - \alpha)] \quad (32)$$

being  $\alpha$  and  $\beta$  the critical exponents. The prime stands for scaled variables, while terms without it are unscaled, or experimental, ones. Finally,  $g$  is the "damping" function proposed by Erickson and Leland:<sup>3</sup>

$$g = \exp \left[ \left( \frac{1}{1 + \nu(\Psi/p_c)^{1/2} + r(\Psi/p_c)^2} \right) \ln \left( 1 + w \left( \frac{p_c}{\Psi} \right)^{\lambda/4} \right) \right]^{-1/\lambda} = \left[ 1 + w \left( \frac{p_c}{\Psi} \right)^{\lambda/4} \right]^{-1/[\lambda(1 + \nu(\Psi/p_c)^{1/2} + r(\Psi/p_c)^2)]} \quad (33)$$

where  $\nu$ ,  $r$ ,  $w$ , and  $\lambda$  are adjustable parameters.

We have used the above transformation of variables together with the Strobridge equation, eq 1. Using the  $A_i$  constants of Table II, we have fitted  $\nu$ ,  $r$ ,  $w$ , and  $\lambda$  to the whole set of  $p$ - $\rho$ - $T$  data of Table I. The best set of parameters was  $\nu = -1.10607$ ,  $r =$



**Figure 3.** Ratio of the residuals of Strobridge equation modified according to Erickson et al. and of the extended and revised equation of Sengers et al. as a function of the reduced density for several isotherms.

0.22770,  $w = 7.007679 \times 10^{-5}$ ,  $\lambda = 0.0967768$ ; Figure 3 shows the ratio of the residuals of the Erickson-Leland-Fox (ELF) EoS to those of the Sengers one in the near-critical region.

The results indicate that the performance of the ELS EoS is very satisfactory in the near-critical region and can be compared to the Sengers EoS in its ability to describe  $p$ - $\rho$ - $T$  data, even improving the results for low values of the reduced density. This is an important result, since the ELF equation reduces to eq 1 far from the CP, and thus it gives quite satisfactory results in regions of the phase diagram for which revised and extended scaling EoS's cannot be applied. Even though it remains to be known whether, much closer to the CP, the ELF EoS still gives good results, it is clear that the EoS would be satisfactory for many engineering applications.

In spite of the good description of the  $p$ - $\rho$ - $T$  surface, again a more extensive analysis of speed of sound or  $C_p$  data is needed before a firm conclusion about the general performance of ELF EoS can be drawn.

Recently, Pitzer and Schreiber<sup>3</sup> (PS) have proposed a classical EoS that is valid except in the very critical region. We have used eq 1 plus the fluctuation contribution proposed by Pitzer and Schreiber<sup>3</sup> (see eq 3 of ref 3). The results indicate that there is no improvement over the results of the Strobridge EoS, and thus we do not describe the PS EoS here. The results agree with the conclusions of Pitzer and Schreiber that their correction term is important only in a very small region around the CP, where the data of Table I are scarce.

## Conclusions

We have obtained an extensive set of  $p$ - $\rho$ - $T$  data in the near-critical region of CHF<sub>3</sub>. The results are consistent with other previously obtained for the classical region. The results have been analyzed in terms of two revised and extended scaling EoS's and show that while both of them lead to similar results near the critical point, the EoS of Sengers et al. seems to be applicable in a  $p$ ,  $\rho$ ,  $T$  range larger than that of Anisimov et al.

Also, two classical EoSs with modified thermodynamic fields have been tested. The results indicate that the Strobridge equation, modified according to the method of Erickson et al., gives results comparable to those of Sengers's EoS in the near critical region, while it reduces to the Strobridge EoS far from the critical point. However, firmer conclusions about this kind of EoS would require  $C_p$  and speed-of-sound data, which are not available for CHF<sub>3</sub>. The EoS proposed by Pitzer and Schreiber has been found to give results that are essentially equivalent to the Strobridge EoS in the region for which  $p$ - $\rho$ - $T$  data are available, the switch to scaling behavior taking place only closer to the critical point.

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