International Journal of Thermophysics, Vol. 14, No. 6, 1993

The Orthobaric Liquid and Vapor Densities of Tetramethylsilane and of 2,2-Dimethylpropane

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Received May 5, 1993

The orthobaric densities of tetramethylsilane and 2,2-dimethylpropane have been measured by means of a hydrostatic density balance. For tetramethylsilane the liquid density has been determined from 289.73 K to the critical point 448.60 K and the vapor density from 353.55 K to the critical point, while for 2,2-dimethylpropane the liquid density has been measured from 290.88 K to the critical point 433.71 K and the vapor density from 349.01 K to the critical point. The results are represented well by the extended-scaling equation of Wegner with three correction terms and the critical indices α, β, and Δ_1, obtained from renormalization-group theory. The fit is not improved by a term expressing an anomaly in the diameter using either of the exponents $(1-\alpha)$ or 2β. The critical density for tetramethylsilane is estimated as $(0.2436 \pm 0.0001)\ \mathrm{g \cdot cm^{-3}}$ and that for 2,2-dimethylpropane as $(0.2318 \pm 0.0001)\ \mathrm{g \cdot cm^{-3}}$.

KEY WORDS: critical phenomena; density; 2,2-dimethylpropane; extended scaling; tetramethylsilane; vapor–liquid equilibrium.

1. INTRODUCTION

The intrinsic interest of the results, the need for the information to assist us in interpreting the results of our determinations of the lower critical end points of solutions of dimethylsiloxane polymers in tetramethyl solvents [1], and a wish to determine the applicability of the extended-scaling equation of Wegner [2] for orthobaric liquid and vapor densities over very wide ranges of temperature have led us to determine the orthobaric liquid densities of tetramethylsilane and 2,2-dimethylpropane from near room

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0195-928X/93/1100-1173$07.00/0

temperature to very near the critical temperature (T_c) and the orthobaric vapor densities from the lowest temperature at which they were measurable with reasonable precision to close to T_c. The densities were determined in a hydrostatic density balance designed and commissioned by Hales of the National Physical Laboratory [3]. The results have been fitted by a variety of equations, chiefly the extended-scaling equation of Wegner. We shall publish elsewhere an analysis of our results for the liquid tetramethylsilane in terms of a phenomenological corresponding-states principle [4], including the dimethylsiloxane oligomers and polymers, after the form introduced by Patterson and Bardin [5]. From the density results we have estimated the critical densities of the two tetramethyls; that for tetramethylsilane agrees very well with the value reported by McGlashan and McKinnon [6]; and that for 2,2-dimethylpropane, although about 3% lower than the value reported by Beattie et al. [7], agrees very well with that reported more recently by Dawson et al. [8].

2. EXPERIMENTS

Both the liquid and the vapor densities were determined by means of an Archimedean hydrostatic density balance whose design and mode of operation have been fully described by Hales [9]. The two-phase fluid sample is kept in a sealed cell and within the midst of one of the phases an iron core enclosed in a silica envelope, known collectively as the bob, is levitated by means of an electronically controlled induced magnetic field. The measured apparent change of weight of the cell on levitation and the known volume of the bob lead to the calculation of the mean density of the fluid in the liquid and the vapor phases and their design has already been described [3]. Each phase was always studied in the presence of a small amount of the other to ensure the orthobaricity of the results. Details of the present form of the apparatus and its manner of use are available elsewhere [10].

3. MATERIALS

Tetramethylsilane (Fluka AG, "purriss," "spectroscopy grade," batch No. 87920) with a stated purity of not less than 99.8 mol% was dehydrated over No. 4 molecular sieves (Sigma Chemical Co.) and distilled through a greaseless Teflon tap into a clean Pyrex glass storage bulb in which it was thoroughly degassed before use. 2,2-Dimethylpropane (Phillips Petroleum Co., "research grade," batch No. 1029) with a stated purity of 99.99 mol%

was used directly, with no additional treatment save the removal of permanent gases after vacuum-line transfer from the original metallic container to a Pyrex glass storage bulb similar to that used for tetramethylsilane.

4. RESULTS

The results of our measurements are given in Table I for tetramethylsilane and in Table II for 2,2-dimethylpropane. Figures 1 and 2 show the

Table I. The Orthobaric Liquid and Vapor Densities d_{liq} and d_{vap} of Tetramethylsilane at Temperatures T; (a) Measured and (b) Calculated from Eq. (3) with Coefficients from Table III

T	d_{liq} or d_{vap} $(\text{g}\cdot\text{cm}^{-3})$		T	d_{liq} or d_{vap} $(\text{g}\cdot\text{cm}^{-3})$	
(K)	(a)	(b)	(K)	(a)	(b)
		Saturated liquid d_{liq}			
289.733	0.64358	0.64365	392.200	0.50395	0.50410
292.193	0.64081	0.64086	397.426	0.49415	0.49433
295.840	0.63667	0.63670	407.960	0.47268	0.47277
303.370	0.62806	0.62801	418.680	0.44718	0.44724
311.240	0.61889	0.61876	423.926	0.43276	0.43278
319.055	0.60949	0.60938	424.048	0.43241	0.43243
327.370	0.59927	0.59916	428.464	0.41881	0.41875
335.720	0.58870	0.58860	433.908	0.39943	0.39919
344.580	0.57711	0.57702	439.600	0.37373	0.37339
353.640	0.56470	0.56470	445.288	0.33434	0.33414
362.588	0.55200	0.55198	447.750	0.29942	0.30008
372.710	0.53670	0.53676	447.838	0.29732	0.29801
383.150	0.51982	0.51991			
		Saturated vapor d_{vap}			
353.550	0.01558	0.01528	429.935	0.09185	0.09171
360.300	0.01819	0.01822	433.080	0.10000	0.10003
367.210	0.02135	0.02162	434.696	0.10485	0.10484
367.323	0.02173	0.02168	441.718	0.13289	0.13273
372.184	0.02429	0.02434	443.547	0.14343	0.14337
376.941	0.02712	0.02718	444.646	0.15128	0.15113
387.186	0.03410	0.03424	445.360	0.15728	0.15702
389.700	0.03600	0.03621	446.021	0.15344	0.16331
397.347	0.04292	0.04286	446.632	0.17025	0.17020
405.436	0.05120	0.05124	447.214	0.17830	0.17826
407.735	0.05408	0.05393	447.365	0.18085	0.18071
413.300	0.06118	0.06115	447.842	0.18954	0.19012
418.556	0.06922	0.06908	448.136	0.19769	0.19814
418.730	0.06932	0.06935	448.332	0.20482	0.20569
424.368	0.07947	0.07947			

experimental points together with the plot of the best fit for both substances. The precision of the results varies across the temperature range and with the nature of the phase under consideration. After taking into account the various possible sources of error, chiefly the precision and accuracy of the balance, the accuracy of calibration of the mass and volume of the bob, and the corrections for diamagnetic repulsion and the compression of the bob, the uncertainty of each individual measurement is believed not to exceed ±0.0002 g · cm^{-3}.

Table II. The Orthobaric Liquid and Vapor Densities d_{liq} and d_{vap} of 2,2-Dimethylpropane at Temperatures T; (a) Measured and (b) Calculated from Eq. (3) with Coefficients from Table IV

T (K)	d_{liq} or d_{vap} (g · cm^{-3})		T (K)	d_{liq} or d_{vap} (g · cm^{-3})	
	(a)	(b)		(a)	(b)
		Saturated liquid d_{liq}			
290.881	0.59300	0.59307	368.318	0.49252	0.49262
292.546	0.59112	0.59119	377.016	0.47813	0.47825
293.020	0.59060	0.59066	387.234	0.45961	0.45975
297.519	0.58552	0.58555	397.407	0.43879	0.43891
301.460	0.58107	0.58102	409.161	0.41005	0.41011
306.220	0.57555	0.57549	413.324	0.39795	0.39800
310.167	0.57092	0.57085	418.804	0.37967	0.37960
314.137	0.56620	0.56612	424.322	0.35646	0.35639
319.113	0.56020	0.56011	430.107	0.32009	0.32005
327.083	0.55036	0.55025	430.028	0.32074	0.32073
333.858	0.54168	0.54162	430.411	0.31738	0.31734
342.423	0.53036	0.53033	430.742	0.31421	0.31421
350.049	0.51987	0.51985	431.167	0.30986	0.30986
357.882	0.50856	0.50858	431.924	0.30061	0.30081
		Saturated vapor d_{vap}			
349.006	0.01862	0.01861	427.907	0.13252	0.13245
353.044	0.02078	0.02067	428.794	0.13778	0.13770
363.493	0.02683	0.02672	430.184	0.14750	0.14745
374.164	0.03410	0.03417	430.311	0.14851	0.14846
385.110	0.04349	0.04363	430.489	0.14995	0.14993
393.251	0.05220	0.05229	430.590	0.15085	0.15078
403.113	0.06536	0.06546	430.835	0.15300	0.15294
408.472	0.07434	0.07438	430.970	0.15418	0.15419
412.516	0.08231	0.08227	431.108	0.15555	0.15550
418.485	0.09670	0.09659	432.252	0.16895	0.16883
422.657	0.10955	0.10951	432.676	0.17569	0.17561
423.395	0.11219	0.11217	433.210	0.18746	0.18763
426.155	0.12358	0.12355			

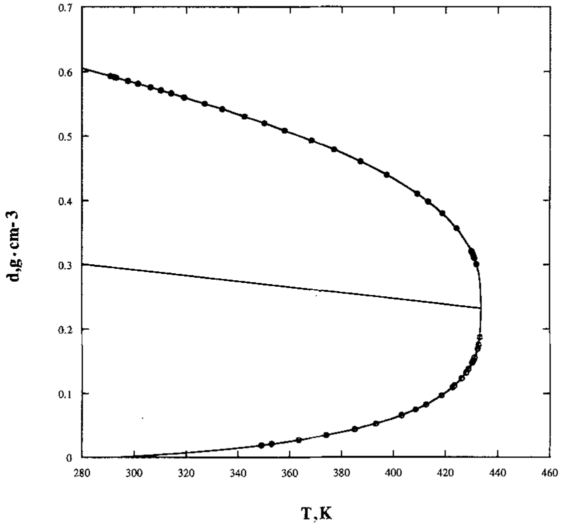

Fig. 1. Orthobaric liquid and vapor densities d_{liq} and d_{vap} for tetramethylsilane as functions of temperature T. The points are experimental and the smooth curve is from Eq. (3) with the coefficients reported in Table III: (—●—) liquid densities; (—○—) vapor densities; and (——) diameter.

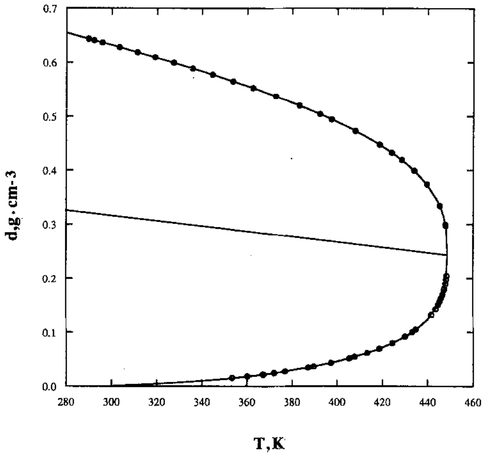

Fig. 2. Orthobaric liquid and vapor densities d_{liq} and d_{vap} for 2,2-dimethylpropane as functions of temperature T. The points are experimental and the smooth curve is from Eq. (3) with the coefficients reported in Table IV: (—●—) liquid densities; (—○—) vapor densities; and (——) diameter.

Anticipating a later discussion based on the fitting procedure discussed in the next section, it may be useful to offer two comments on our results. The first is that there is greater scatter in our determinations of d_{vap} than in those of d_{liq}. This is perhaps unsurprising given the lower densities and hence the smaller difference of the measured masses in the levitated and unlevitated bob that relates to the fluid density. In a later paper we explore the possibility of calculating virial coefficients from the results of our measurements of d_{vap}. The second comment is merely that our measurements for 2,2-dimethylpropane are subject to less scatter than those for tetramethylsilane and this is probably due largely to improved familiarity with the density balance. We comment on the agreement of our results with those of other workers in a later section.

5. DATA ANALYSIS

5.1. Fitting Procedure

It is now well-known that the simple asymptotic expression, $\Delta d = B\varepsilon^{\beta}$, for the dependence of the difference between the densities of the coexisting phases of a pure fluid, $\Delta d = (d_{\text{liq}} - d_{\text{vap}})$, on the reduced temperature difference, $\varepsilon = (1 - T/T_c)$, holds only in the immediate vicinity of the critical point. To extend the validity of this expression ouside the critical region, Wegner [2] and Ley-Koo and Green [11] proposed an expansion of the form

$$\Delta d/d_c = k_2 \varepsilon^{\beta} + k_3 \varepsilon^{\beta+\Delta_1} + k_4 \varepsilon^{\beta+2\Delta_1} + \cdots \qquad (1)$$

where $k_3 \varepsilon^{\beta+\Delta_1}$ and $k_4 \varepsilon^{\beta+2\Delta_1}$ are called the first and second scaling correction terms, respectively, each characterized by a universal "gap" exponent, Δ_1. Scaling theory [11, 12] also suggests that the diameter of the coexistence curve, i.e. the average value of the order parameter in the coexisting phases, obeys

$$(d_{\text{liq}} + d_{\text{vap}})/2 = 1 + k_1 \varepsilon + k_7 \varepsilon^{1-\alpha} + k_8 \varepsilon^{1-\alpha+\Delta_1} + \cdots \qquad (2)$$

where α is the critical exponent for the divergence of the constant-volume specific heat for a pure substance at its critical point and $k_7 \varepsilon^{1-\alpha+\Delta_1}$ are again correction terms. The first term, $k_7 \varepsilon^{1-\alpha}$, is commonly known as the "anomalous-diameter" term because of the curvature it imparts to a line long believed to be straight. Experimental evidence for the significance of this term is scarce because since α is small, 0.11 approximately, the anomaly is small and experimentally accessible only very close to the critical point.

In this investigation the densities of the coexisting liquids and vapor phases could not be determined at exactly the same temperatures; thus our results do not embrace the canonical pairs necessary for the direct calculation of Δd. Accordingly, for fitting purposes we turned to a procedure devised earlier in this laboratory [13] to meet the analogous problem of fitting liquid–liquid coexistence curves to similar expressions whereby Eqs. (1) and (2) were combined to give for d_{liq},

$$\begin{aligned} d_{\text{liq}} = {} & d_c + C\varepsilon + C_1\varepsilon^{1-\alpha} + C_2\varepsilon^{1-\alpha+\Delta_1} + \cdots \\ & + (\tfrac{1}{2})(B\varepsilon^{\beta} + B_1\varepsilon^{\beta+\Delta_1} + B_2\varepsilon^{\beta+2\Delta_1} + B_3\varepsilon^{\beta+3\Delta_1} + \cdots) \end{aligned}$$

and for d_{vap}

$$\begin{aligned} d_{\text{vap}} = {} & d_c + C\varepsilon + C_1\varepsilon^{1-\alpha} + C_2\varepsilon^{1-\alpha+\Delta_1} + \cdots \\ & - (\tfrac{1}{2})(B\varepsilon^{\beta} + B_1\varepsilon^{\beta+\Delta_1} + B_2\varepsilon^{\beta+2\Delta_1} + B_3\varepsilon^{\beta+3\Delta_1} + \cdots) \end{aligned} \quad (3)$$

where d_c is the critical density and the B_i and C_i are coefficients, or amplitudes, to be determined by experiment. The densities for each substance were fitted to various truncated forms of Eq. (3) by means of a computer program based on Bevington's nonlinear fitting routine, CURFIT [14]. The benefit of including various terms was followed by the sharp drop in the reduced χ^2, χ_ν^2, given by

$$\chi_\nu^2 = \chi^2/\nu = (1/\nu) \sum (d_{\text{obs}} - d_{\text{calc}})^2/\omega_i$$

where $\omega_i = 1/\sigma_i^2$ is the weight of the ith point and ν is the number of degrees of freedom, the difference between the number of data points and the number of fitted parameters. The average standard deviaton σ is given by $\sigma = \sum \sigma_i$/number of data pairs and σ_i, the deviation for each point in the independent variable, takes into account the uncertainty in the independent variable calculated by the propagation of errors.

5.2. Fixed Parameters

The constants appearing in Eq. (3) fall into three groups: (i) those determined conveniently by direct measurement, (ii) those evaluated by theory, and (iii) those that can be obtained only from the results of experiment by curve fitting. The critical temperature essentially falls into group i, although some refinement of the final value is sometimes desirable; the critical indices α, β, and Δ_1 fall into group ii; and the remaining parameters and amplitudes d_c, B_i, and C_i all emerge from the fitting procedure. We discuss each of these classes of parameter separately.

Initially we adopted for the critical temperatures the then-most-recently reported values, namely, (448.64 ± 0.01) K for tetramethylsilane by McGlashan and McKinnon [6] and (433.78 ± 0.05) K for 2,2-dimethylpropane by Eubank *et al.* [15]. However, a free fit of the densities for both substances to the full form of Eq. (3) using these values indicated optimized values for β of 0.344 for tetramethylsilane and 0.351 for 2,2-dimethylpropane, singificantly different from the value 0.325 predicted by the renormalization group theory discussed below. In the knowledge that the latter value of β is now widely regarded as correct, we sought the effect of varying T_c for each substance with β fixed at the 0.325 to determine whether an optimum T_c could be found within the published experimental error, which would produce an equally low value of χ_ν^2 as that with the free-fit value. It emerged that the fit with $\beta = 0.325$ exhibited equally acceptable χ_ν^2 for tetramethylsilane with $T_c(\text{opt}) = 448.60$ K, just outside the (448.64 ± 0.01) K of McGlashan and McKinnon, and for 2,2-dimethylpropane $T_c(\text{opt}) = 433.71$ K, again just outside the (433.78 ± 0.05) K of Eubank et al. Accordingly, despite the difference from the experimental T_c, we adopted these effective values of T_c in all the subsequent data analysis, implicitly suggesting that our material or our temperature scales differed slightly from those of the workers cited. The alternative procedure for checking T_c that we have used elsewhere [13] for orthobaric mixtures very close to critical end points, which depends on identifying the asymptotic critical region, could not be employed here because (i) we had few data points sufficiently close to T_c and (ii) this requirement, which amounts to a specification of the extent of the asymptotic critical region, is harder to meet for pure substances than for mixtures for which, apparently, this region is larger.

As mentioned above, the renormalization-group theory has yielded values for the critical exponents of three-dimensional Ising-like systems which are now believed accurate. We therefore regard these parameters not as adjustable, and thus to be evaluated by our fitting routine, but rather as known quantities and we have adopted the theoretical estimates of Le Guillou and Zinn-Justin [16]:

$$\alpha = 0.1100 \pm 0.0045$$

$$\beta = 0.3250 \pm 0.0015$$

$$\Delta_1 = 0.4980 \pm 0.0200$$

We turn now to the evaluation of the critical density and the amplitudes in Eq. (3).

5.3. Results of the Fitting Procedure

With the fixed values for T_c, α, β, and Δ_1 given above, we employed CURFIT to identify the form of Eq. (3) with the most appropriate set of correction terms and to evaluate the corresponding critical densities d_c and the amplitudes B_i and C_i. The effect of taking different numbers of fitting parameters in Eq. (3) can be seen from Tables III and IV, wherein are listed a number of combinations of Wegner coexistence-curve correction terms and various forms of linear, curved, or Wegner-corrected diameter terms. The results are listed in order of diminishing χ_ν^2 for the sake of easier interpretation. A number of simple conclusions emerge.

(i) The best overall fit for both tetramethylsilane and 2,2-dimethylpropane incorporating the renormalization group theory values of the critical exponents is fit 8 with with three Wegner coexistence curve correction

Table III. Nonlinear Least-Squares Fitted Coefficients for the 54-Point Data Set of Orthobaric Tetramethylsilane Densities to Eq. (3) for T_c Fixed at 448.60 K and $\beta = 0.325$, $\alpha = 0.11$, and $\Delta_1 = 0.498$[a]

	$g \cdot cm^{-3}$								
Fit	d_c	B	C	B_1	C_1	C_2	B_2	B_3	χ^2
1	0.24473 (0.00005)	0.90985 (0.0001)	0.21046 (0.0003)						51
2	0.24481 (0.00001)	0.90051 (0.00004)	0.20713 (0.00005)	0.02438 (0.00008)					43
3	0.24439 (0.00008)	0.89897 (0.0005)	0.15993 (0.0078)	0.02927 (0.0010)	0.04134 (0.007)				43
4	0.24592 (0.00011)	0.89621 (0.0005)	1.12478 (0.0490)	0.03838 (0.0014)	−0.59777 (0.033)	−0.38767 (0.02)			37
5	0.24369 (0.00005)	0.86341 (0.0010)	0.21955 (0.0004)	0.25922 (0.0060)			−0.33260 (0.008)		9.1
6	0.24448 (0.00008)	0.86180 (0.0010)	0.32423 (0.0087)	0.27994 (0.0060)	−0.09025 (0.007)		−0.37705 (0.008)		6.3
7	0.24308 (0.00014)	0.85306 (0.0012)	−0.51673 (0.0641)	0.34747 (0.0080)	0.046013 (0.0423)	0.35751 (0.03)	−0.49110 (0.012)		2.7
8	0.24365 (0.00006)	0.83739 (0.0016)	0.21902 (0.0004)	0.54995 (0.0150)			−1.24426 (0.040)	0.85251 (0.040)	0.76
9	0.24364 (0.00010)	0.83731 (0.0018)	0.21788 (0.0109)	0.55084 (0.0176)	0.00097 (0.0093)		−0.24728 (0.054)	0.85578 (0.0524)	0.78

[a] The uncertainties of the values are shown in parentheses.

terms and a linear diameter. The average standard deviation of the fit is similar to the expected experimental uncertainty, $\pm 0.00002\ \mathrm{g \cdot cm^{-3}}$. However, this improvement in the goodness of fit by adding Wegner correction terms to the coexistence curve is obtained at the cost of introducing "wiggles" in the predicted densities. This is illustrated in Fig. 3 and 4, which show the deviation $\{d(\mathrm{exp}) - d(\mathrm{calc})\}$, with $d(\mathrm{calc})$ the density calculated from fit 8 to Eq. (3), as functions of T for both tetramethylsilane and 2,2-dimethylpropane. With less good fits than fit 8 the periodic deviations are even more pronounced. It is obvious that there are systematic deviations which increase as the number of C_i terms increases.

(ii) The fitting procedure is strikingly sensitive to the details of the exact values of some of the fitting parameters, although as Tables III and IV show, the value of d_c changes surprisingly little with the current form

Table IV. Nonlinear Least-Squares Fitted Coefficients for the 53-Point Data Set of Orthobaric 2,2-Dimethylpropane Densities to Eq. (3) for T_c Fixed at 433.71 K and $\beta = 0.325$, $\alpha = 0.11$, and $\Delta_1 = 0.498$[a]

	$\mathrm{g \cdot cm^{-3}}$								
Fit	d_c	B	C	B_1	C_1	C_2	B_2	B_3	χ^2
1	0.23242 (0.00004)	0.85054 (0.0002)	0.19448 (0.0003)						82
2	0.23254 (0.00004)	0.83109 (0.00004)	0.18465 (0.00004)	0.05542 (0.00010)					37
3	0.23161 (0.00007)	0.82765 (0.0005)	0.05293 (0.0082)	0.06773 (0.0010)	0.11405 (0.010)				32
4	0.23329 (0.00011)	0.82544 (0.0005)	1.09238 (0.0583)	0.07484 (0.0010)	−0.57495 (0.040)	−0.41722 (0.02)			26
5	0.23180 (0.00005)	0.80389 (0.0008)	0.19581 (0.0005)	0.25326 (0.0050)			−0.30306 (0.010)		5.5
6	0.23235 (0.00007)	0.80142 (0.0008)	0.29565 (0.0105)	0.28060 (0.0060)	−0.08468 (0.010)		−0.35892 (0.010)		3.6
7	0.23125 (0.00013)	0.79638 (0.0010)	−0.43792 (0.0738)	0.32969 (0.0080)	0.039202 (0.050)	0.31915 (0.03)	−0.45076 (0.010)		1.5
8	0.23182 (0.00005)	0.78526 (0.0014)	0.19524 (0.0005)	0.49124 (0.0160)			−1.09935 (0.050)	0.77767 (0.050)	0.15
9	0.23191 (0.00008)	0.78580 (0.0015)	0.21118 (0.0123)	0.48363 (0.0168)	−0.01349 (0.011)		−1.06822 (0.056)	0.73859 (0.0574)	0.11

[a] The uncertainties of the values are shown in parentheses.

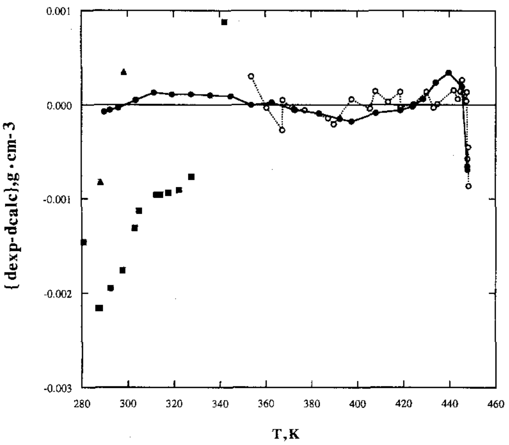

Fig. 3. Density deviation plots $\{d_{\mathrm{exp}} - d_{\mathrm{calc}}\}$ as functions of temperature T for tetramethylsilane with d_{calc} calculated from Eq. (3) with the parameters of fit 8 in Table III. The filled symbols refer to liquid densities and the open symbols to vapor densities: (—○—) results reported in this paper; (□) Yokoyama et al. [20]; (△) García Baonza et al. [21].

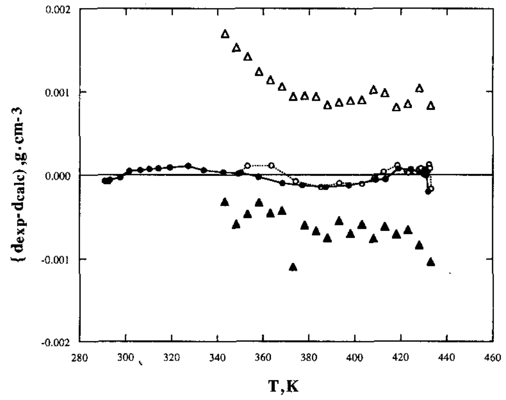

Fig. 4. Density deviation plots $\{d_{\mathrm{exp}} - d_{\mathrm{calc}}\}$ as functions of temperature T for 2,2-dimethylpropane with d_{calc} calculated from Eq. (3) with the parameters of fit 9 in Table IV. The filled symbols refer to liquid densities and the open symbols to vapor densities: (—○—) results reported in this paper; (△) Dawson et al. [8].

of Eq. (3). The influence of the choices of the critical temperature and the critical exponents has been discussed above. It is perhaps just worthwhile to comment that the Wegner coexistence-curve correction terms do not form a convergent series except close to the critical point. Indeed, it is clear that $(B_1 + B_2 + B_3) \sim 0$; for example, for fit 8 the sum of the amplitudes is 0.15820 for tetramethylsilane and 0.16956 for 2,2-dimethylpropane. In all these fits the values of the corresponding amplitudes are similar for each substance. This may reflect more the molecular similarity of these substances and their obedience to a principle of corresponding states rather than something deeper concerning the nature of the amplitudes.

(iii) The effect of an anomalous $C_1 e^{1-\alpha}$ term in the diameter was analyzed at every step in the fitting procedure. However, no unambiguous evidence was found for improvement in the fit by the inclusion of either this term or this term plus the next one in the same branch of Eq. (2), $C_2 e^{1-\alpha+\Delta_1}$. This is unsurprising since the anomaly in the diameter is expected to be significant only very close to T_c and the large range of our data makes it unlikely that it could be detected. Fit number 9 in Tables III and IV shows the effect of including a curved diameter term. The effect is small and is, in part, the consequence of the small number of data points very close to T_c, say within 2–3 K. The deviation plots of $\{d(\exp) - d(\text{calc})\}$ for both tetramethylsilane and 2,2-dimethylpropane show it to be negative very close to T_c, reflecting indistinguishably either the influence of gravitational compressibility on the contents of our cells, which were about 60 mm high with a 40-mm bob for the liquid cells and 80 mm high with the same bob for the vapor cells, or the effects of filling to other than the critical density overall.

(iv) The alternative question [17, 18] about the desirability of employing a similar term with the $(1-\alpha)$ exponent in the C_1 and C_2 terms replaced by 2β was not explored, since if the inclusion of the terms with $(1-\alpha) = 1 - 0.11 = 0.89$ leads to no improvement in the fit, then it is unlikely that terms with an exponent $2\beta = 0.65$ would do better. In these circumstances we have therefore nothing to say concerning the desirability of replacing $\varepsilon^{(1-\alpha)}$ by $\varepsilon^{2\beta}$ in Eq. (2). Further details on this point are described by Balzarini et al. [19].

(v) The best overall fit was obtained with the scaling relation with three Wegner correction terms with the coefficients given under fit 8 in Tables III and IV.

6. CONCLUSIONS

We believe that our results suffer a little from density gradients except when closest in temperature to T_c, partly on account of the relatively large magnitude of ε and partly because although, as Hales and Gundry showed, changes in weight in the bob can be observed when moving the position of the bob while remaining wholly within the phase under examination, none were observed in this work. This may be due to our failure to quite achieve the optimum initial loading of the sample cell and thus to nearly enough approach the critical density.

The most recently published densities of tetramethylsilane are those of Yokoyama et al. [20] and García Baonza et al. [21]. They are shown in the deviation graph (Fig. 3). There is clearly a significant deviation from our results and those of Yokoyama et al. but those of García Baonza et al. are, although in the main extending over a range at lower temperatures than our results, in good agreement. The best previously published densities for 2,2-dimethylpropane are those of Dawson et al. [8]. They are shown on the deviation graph (Fig. 4). They are in essentially good agreement with our results.

No direct measurement of the critical density of tetramethylsilane has been reported previously. McGlashan and McKinnon [6] calculated its critical molar volume V_c by extrapolating to T_c a plot of the orthobaric molar volumes of the liquid and vapor phases against temperature. They reported for V_c a value of $(361 \pm 8)\,\mathrm{cm^3 \cdot mol^{-1}}$, which yields $d_c = (0.2444 \pm 0.0053)\,\mathrm{g \cdot cm^{-3}}$, in excellent agreement with the critical density of tetramethylsilane calculated from our results, i.e., $(0.2436 \pm 0.0001)\,\mathrm{g \cdot cm^{-3}}$. The critical density of 2,2-dimethylpropane is found to be $(0.2318 \pm 0.0006)\,\mathrm{g \cdot cm^{-3}}$; and although this value is in excellent agreement with the value of $(0.2318 \pm 0.0021)\,\mathrm{g \cdot cm^{-3}}$ estimated from the 38 data points on the diagram of the orthobaric densities of Dawson et al. [8], it falls about 3% below the much earlier value of $0.238\,\mathrm{g \cdot cm^{-3}}$ reported by Beattie et al. [7]. A full analysis of the results of Dawson et al. using Eq. (3) produced very similar results to those which emerged from the analysis of our measurements, both in the optimum number of terms needed to describe the results adequately and in the values of the coefficients. In particular, the estimated critical density $0.23189\,\mathrm{g \cdot cm^{-3}}$ differed inappreciably from our value, $0.23182\,\mathrm{g \cdot cm^{-3}}$.

The Wegner expansion was tested over very wide ranges of temperatures; indeed, we are unaware of any more searching test of it for either pure or mixed fluid systems. The maximum values for the reduced difference in temperature from the critical point ε were 0.329 for 2,2-dimethylpropane and 0.354 for tetramethylsilane and for a density range up to 155% of the critical density for 2,2-dimethylpropane and 164% for tetramethylsilane. For both substances the densities of both liquid and vapor were very well represented by the scaling relation with three Wegner correction terms. As expected in view of the large temperature range of the results, the diameters revealed no anomalous behavior.

ACKNOWLEDGMENTS

We gratefully acknowledge the receipt of a Grant-in-Aid from the Royal Society that enabled the purchase of the density balance from the National Physical Laboratory on the demise of the Division of Chemical Standards and the unstinted advice and encouragement that were received both then and later from Dr. John Hales, formerly of the Division of Mechanical and Optical Metrology of the National Physical Laboratory. J.-M. B.-C. acknowledges with thanks the receipt of a scholarship from the Consejo Nacional de Ciencia y Tecnología, México, and financial support from the Universidad Autónoma de Neuvo León, Monterrey, México.

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