# Experimental Evidence for a Departure from the Law of the Rectilinear Diameter*

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(Received 22 January 1974)

We have determined the relative liquid and vapor densities $\rho_L/\rho_c$ and $\rho_V/\rho_c$ along the coexistence curve in $SF_6$ using capacitance measurements of the dielectric constant together with an independent determination of the dielectric-constant–density relationship. Near the critical point, the diameter $\rho_d = \frac{1}{2}(\rho_L + \rho_V)$ exhibits a successively larger departure from the extrapolated linear dependence on temperature. This feature is characteristic of many liquid-vapor critical-point models, but it has not been previously observed.

The law of the rectilinear diameter, first proposed in 1886,[1] relates the densities of the coexisting liquid ($\rho_L$) and vapor ($\rho_V$) phases of a fluid near its critical point to the temperature,

$$\rho_d = \tfrac{1}{2}(\rho_L + \rho_V) = \rho_c + a(T_c - T), \qquad (1)$$

where $\rho_c$ and $T_c$ are the critical density and temperature of the fluid and $a$ is a constant. Data for a number of fluids obey Eq. (1) to within experimental error.[2-6]

Recently, interest in the law of the rectilinear diameter has been renewed as a result of several model calculations predicting deviations from the law. All of the calculations such as those based on Widom and Rowlinson's penetrable-sphere model,[7] Mermin's bar[8] and decorated lattice-gas[9] models, and Hemmer and Stell's continuum model[10] suggest that the slope of the diameter should diverge in proportion to the specific heat at constant volume $C_V$,

$$-(1/\rho_c)d\rho_d/dT = bC_V. \qquad (2)$$

This result has also been obtained on the basis of thermodynamic arguments by Green, Cooper, and Levelt Sengers[11] and by Mermin and Rehr.[12]

Several experimental searches for the deviation have been reported.[2-6] Of these, the data on $CO_2$ analyzed by Levelt Sengers, Straub, and Vicentini-Missoni[4] have the combination of precision and proximity to the critical point most appropriate for revealing a deviation. They conclude that the largest departure from Eq. (1) consistent with their data amounts to 0.3% of the critical density. Zollweg and Mulholland[6] point out, however, that on the basis of an extension of the decorated lattice-gas model the maximum deviation is expected to lie between 0.1 and 0.3% of $\rho_c$. The present paper reports the first results with sufficient precision to reveal such detail. We find in $SF_6$ a deviation of about 0.5% whose character is consistent with Eq. (2).

The densities reported here were determined from capacitance-bridge measurements of the dielectric constant $\epsilon$. The relationship between $\epsilon$ and the density at a temperature 2.831°C above $T_c$ was determined in a separate experiment[13] rather than relying on the Clausius-Mossotti equation. In addition, the temperature dependence of $\epsilon$ for $SF_6$ at $0.995\rho_c$ and $0.028 \leq T - T_c \leq 13.2$°C was investigated. Any critical anomaly in $\epsilon$ is expected to depend upon the correlation length $\xi$. At $T - T_c = 0.028$°C we have[14] $\xi = 790$ Å whereas at $T_c - T = 0.020$°C $\xi$ is estimated to be 385 Å.[15] Therefore, we expect that if there is a critical anomaly in $\epsilon$ its effect will be greater at $T - T_c = 0.028$°C than at $T_c - T = 0.020$°C. Since the maximum change in $\epsilon$ due to the presence of the critical point consistent with our data above $T_c$ corresponds to $5\times10^{-4}\rho_c$, we believe that our density measurements below $T_c$ include a maximum error of $5\times10^{-4}\rho_c$ due to a possible anomaly in $\epsilon$. Such an error is too small to invalidate our observation of a deviation from the law of the rectilinear diameter. A theoretical prediction suggests that any critical-point anomaly is smaller than we allow for.[16] In this analysis we have assumed that the polarizability of $SF_6$ has a negligible temperature dependence below $T_c$.

As there are several difficulties in making precise dielectric-constant measurements near the critical point, we discuss some features of the experimental apparatus. A sample of instrument-grade $SF_6$ from Matheson Chemical Co. (<100 ppm impurities) was contained in a copper cell whose temperature was stabilized to better than 0.001°C. The temperature was measured relative to $T_c$ using a calibrated thermistor. The cell was fitted with windows allowing direct observation of the meniscus and measurement of its height relative to the capacitor assembly.

The capacitance measuring probe consisted of a stack of nine polished stainless-steel disks 1 mm thick and 19 mm in diameter. Thus eight separate capacitors were formed but the results reported here are for only five. An internal short that developed during the course of the experiment prevented the use of the remaining three. Each disk was separated and insulated from the disk above and below by small glass spacers 0.20 mm thick. Shielded capacitance measurements were made at a frequency of 10 kHz by connecting two adjacent plates to the capacitance bridge (ESI model 701) while grounding the surrounding plates and cell. By using each successive pair of plates we thus obtained the dielectric constant at five different vertical heights in the cell. Each capacitor was calibrated both in vacuum and while immersed in dried $CCl_4$. After calibration the cell was filled with $SF_6$; at all temperatures below $T_c$ some of the plates were in the liquid and some in the vapor. The error in density measurements due to all causes is estimated to be less than $10^{-3}\rho_c$.

Near the critical point it was necessary to correct the density measurements from each capacitor to account for the variation of density with height. The $\rho_L$ and $\rho_V$ appearing in Eq. (1) represent the densities at the interface between the coexisting phases. Because of the diverging compressibility of the fluid, Earth's gravitational field produces a large vertical density gradient. The density at height $h$ above the meniscus was corrected to the density at the meniscus using the relation $d\rho = (\partial\rho/\partial h)_T dh = -g(\partial\rho/\partial\mu)_T dh$. Here $g$ is the acceleration of gravity and $\mu$ is the chemical potential per unit mass. The measured value

$$\left(\frac{\partial\rho}{\partial\mu}\right)_T = 1.67\times10^{-10}\left(1-\frac{T}{T_c}\right)^{-1.225} \mathrm{g^2/erg\ cm^3}$$

is the same in both phases.[15]

The results of a series of measurements made during two sweeps in increasing temperatures and two in decreasing temperatures over an 8-month period are shown in Fig. 1. Here we plot $\rho_d$ obtained from the dielectric-constant measurements as described above as a function of $T_c - T$. The straight line represents a least-squares fit to the data at temperatures more than 3°C below $T_c$. The data depart significantly from the line in the immediate vicinity of $T_c$ as is shown in greater detail in Fig. 2. The deviation from the rectilinear diameter has a maximum value of $5\times10^{-3}\rho_c$.

While the magnitude of the effect we see is about that to be expected from the model calculations, it is sufficiently small that its origin could come from several effects unrelated to the density. These include the following:

(1) Nonequilibrium conditions in the $SF_6$. This is unlikely as we made observations as a function of time at each new temperature. Data were taken only after the capacitance had reached a stable value. Near $T_c$ waiting periods of 5 d were necessary. Further, data taken following a temperature increase agreed within experimental limits with data at the same temperature taken after a temperature decrease.

(2) Electroconstriction. A calculation shows that this effect would contribute at most $\Delta\rho = 4\times10^{-6}\rho_c$ to our measurements.[18] As expected from this calculation, we found no effect on the measured capacitance due to changing the bridge voltage.

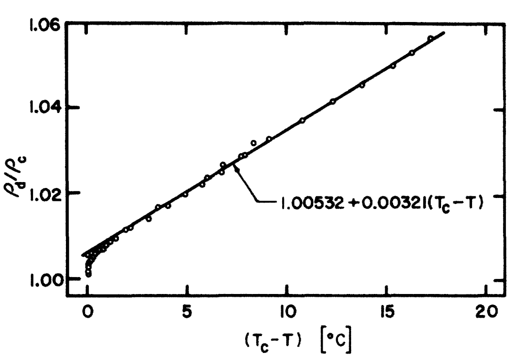


FIG. 1. The density diameter as a function of temperature for $SF_6$. The straight line represents a least-squares fit to the data for $T_c - T$ greater than 3°C.

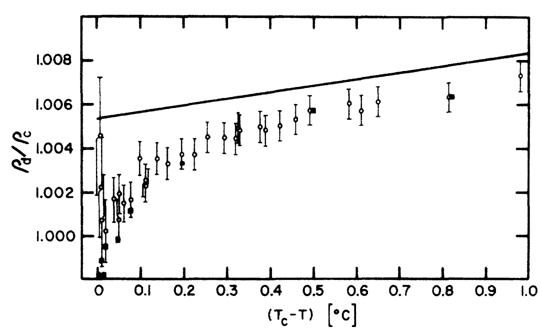


FIG. 2. The data of Fig. 1 at temperatures near $T_c$. The straight line is the line shown in Fig. 1. The error bars include half the gravitational correction at all temperatures. The apparent rise in $\rho_d$ very close to $T_c$ is caused by the linear extrapolation we have used to make gravitational corrections (Ref. 17). The solid squares correspond to data analyzed without making gravitational corrections.

(3) Thin-sample effects. Since the sample is the fluid contained between two capacitor plates, we might expect to observe density differences when the correlation length is comparable to the sample thickness.[19] At $T_c - T = 0.020°C$, the smallest value for which we have reliable data, the correlation length is about 385 Å,[14,15] a factor of 6500 less than the plate separation. Thus we believe that our measurements yield the bulk density.

Comparison of our results to Eq. (2) is complicated by the absence of $C_V$ measurements for $SF_6$. We can, however, estimate $C_V$ in two ways: first, by substituting measured values into the relation

$$C_V = \frac{TV(\partial P/\partial T)_V^2}{\rho v_S^2 - 1/\kappa_T},$$

where $v_S$ is the sound velocity and $\kappa_T$ the isothermal compressibility,[20] and second, by using the measured values of $C_V$ in $CO_2$[21] and a corresponding-states argument. The values of $d\rho_d/dT$ were obtained graphically from a smooth line drawn through the data of Fig. 2. Within experimental error, Eq. (2) was obeyed with a value of $b = (1.6 \pm 0.8)\times 10^{-3}$ mole/cal when the sound-velocity estimate of $C_V$ was used and $b = (0.85 \pm 0.4)\times 10^{-3}$ mole/cal for the corresponding-states estimate. Widom and Rowlinson[7] predict $b = 1/2RT_c = 0.78 \times 10^{-3}$ mole/cal. The comparison must be considered to be satisfactory in light of the uncertainties both in the values of $d\rho_d/dT$ and in the values of $C_V$.

Since submitting this manuscript, Gopal *et al.*[22] have reported observation of a deviation from the law of the rectilinear diameter for the binary mixture carbon disulfide and nitromethane. They observe an effect qualitatively similar to that reported here.

We would like to thank J. Flanigan for technical assistance and Dr. B. Widom and Dr. H. Meyer for helpful discussions.

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*Based on the Ph. D. thesis of J. Weiner; work supported in part by the National Science Foundation under Grant No. GP-28325.

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[1]L. Cailletet and E. C. Mathias, C. R. Acad. Sci., 102, 1202 (1886), and 104, 1563 (1887).

[2]R. K. Teague and C. J. Pings, J. Chem. Phys. 48, 4973 (1968).

[3]L. A. Weber, Phys. Rev. A 2, 2379 (1970).

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

[5]A. B. Cornfeld and H. Y. Carr, Phys. Rev. Lett. 29, 28 (1972).

[6]J. A. Zollweg and G. W. Mulholland, J. Chem. Phys. 57, 1021 (1972).

[7]B. Widom and J. S. Rowlinson, J. Chem. Phys. 52, 1670 (1970).

[8]N. D. Mermin, Phys. Rev. Lett. 26, 169 (1971).

[9]N. D. Mermin, Phys. Rev. Lett. 26, 957 (1971).

[10]P. C. Hemmer and G. Stell, Phys. Rev. Lett. 24, 1284 (1970), and J. Chem. Phys. 56, 4274 (1972).

[11]M. S. Green, M. J. Cooper, and J. M. H. Levelt Sengers, Phys. Rev. Lett. 26, 492 (1971).

[12]N. D. Mermin and J. J. Rehr, Phys. Rev. Lett. 26, 1155 (1971).

[13]J. Weiner, K. H. Langley, and N. C. Ford, Jr., to be published. Our basic conclusion regarding the deviation from the rectilinear diameter is unchanged if we use the Clausius-Mossotti relation to analyze our data, but the numerical constants are slightly altered.

[14]V. G. Puglielli and N. C. Ford, Jr., Phys. Rev. Lett. 25, 143 (1970).

[15]T. T. Feke, J. B. Lastovka, G. B. Benedek, K. H. Langley, and P. B. Elterman, Opt. Commun. 7, 13 (1973).

[16]S. Y. Larsen, R. D. Mountain, and R. Zwanzig, J. Chem. Phys. 42, 2187 (1965).

[17]We are indebted to T. Charlton for providing us with his unpublished results of a computer analysis based on the Stony Brook equation of state. These calculations show that for $T_c - T > 0.020°C$ the maximum error our analysis will contribute is $-8\times 10^{-4}$ in $\rho_d/\rho_c$. Closer to $T_c$, however, the error becomes increasingly large and positive leading to the upturn near $T_c$.

[18]H. S. Frank, J. Chem. Phys. 23, 2023 (1954).

[19]M. E. Fisher and M. N. Barber, Phys. Rev. Lett. 28, 1516 (1972).

[20]R. Mohr, Ph. D. thesis, University of Massachusetts, 1972 (unpublished), has made this estimate.

[21]J. A. Lipa, C. Edwards, and M. J. Buckingham, Phys. Rev. Lett. 25, 1086 (1970).

[22]E. S. R. Gopal, R. Ramachandra, P. Chandra Sekhar, K. Govindarajan, and S. V. Subramanyam, Phys. Rev. Lett. 32, 284 (1974).