We should expect to observe these effects whenever the absorptive optical potential is strong enough to produce a division into inner and outer states.

To the best of our knowledge, the existence of inner states has not previously been discussed. Of course, any exact solution of the wave equation for the usual problems automatically takes them into account. We hope to study further their physical significance and implications for other experiments.

We wish to thank Professor Max Krell for stimulating discussions and for sending us a preprint of his work. We also thank Professor Robin Tucker for the use of his search program. The computations were performed at the University of Massachusetts Research Computing Center with the aid of a grant from the University.

*Research supported in part by the National Science Foundation.

[1]M. Krell, Phys. Rev. Lett. 26, 584 (1971).

[2]These results are obtained by an expansion in powers of the penetration of $\Psi_0$ into the inner region. They are not an expansion of powers of $V_R$. Since the Hamiltonian is not Hermitian, its eigenstates are not necessarily orthogonal; this complication does not affect our qualitative discussion.

[3]This can be derived using projection-operator techniques. See H. Feshbach, Ann. Phys. (New York) 5, 537 (1958), and 19, 287 (1962).

# Temperature Dependence of Critical Opalescence in Carbon Dioxide*

John A. White and Bruce S. Maccabee
*American University, Washington, D. C. 20016*
(Received 29 March 1971)

Rayleigh scattering has been studied along the critical isochore and the coexistence curve of carbon dioxide. Measured intensities interpreted according to the theory of Ornstein and Zernike agree with expectation based on classical *PVT* measurements. It is suggested that over many decades of temperature distance from $T_c$ the *PVT* and optical data are consistent with a reduced compressibility $(\partial\rho/\partial\mu)_T = \Gamma t^{-\gamma}$, and $\Gamma'(-t)^{-\gamma'}$, with $t = (T-T_c)/T_c$, where $\gamma = 1.17 \pm 0.02 = \gamma'$ and $\Gamma = 0.072 \pm 0.006 = 4.1\Gamma'_{\text{gas}} \simeq 3.6\Gamma'_{\text{liq}}$.

Data have been obtained on the intensity of critical opalescence in carbon dioxide in the supercritical phase along the critical isochore for $T > T_c$ and in the gas and liquid phases close to the coexistence line for $T < T_c$. Intensities were measured for light of wavelength 0.633 $\mu$m, scattering angles of 13.5 and 22.5°, and temperatures in the range $10^{-3} \leq |T-T_c| \leq 10$°C.

Measurements were made on $CO_2$ contained in a scattering cell constructed of stainless steel, with indium and lead seals. It had plane, parallel sapphire windows 5 mm apart which were antireflection coated and oriented so as not to depolarize light. No depolarization was observed with this cell upon filling it to nearly the critical pressure of $CO_2$. The volume of the cell was adjusted so that at $T_c$ the meniscus appeared at the center. The position of the cell (its height) could be adjusted relative to the incident beam of light to obtain scattering from above, below, or at the meniscus. A narrow beam of light (~0.1 mm diam) from a 4-mW He:Ne laser was used to illuminate the gas in the cell. The intensity of the light was attenuated, for measurements close to $T_c$, using neutral density filters.

Intensities of the incident and scattered light were measured with an RCA 7265 photomultiplier. The photomultiplier was calibrated by an addition method: Two small light bulbs were placed close together relatively far from an aperture in front of the photomultiplier; the intensities of the two bulbs were made equal as measured by the photocurrent, then added to give a reading for double intensity. The intensity was doubled repeatedly this way to calibrate the photomultiplier over eight decades of intensity. The calibration thus obtained agreed with one based on an assumed linearity of photocurrents below $10^{-7}$ A and with a calibration based on neutral density filters whose densities were checked by precision densitometers.

The temperature of the cell was controlled to $\lesssim 3\times10^{-4}$°C, with thermal gradients $\lesssim 0.1$ mdeg/cm. Temperatures were measured with a platinum resistance thermometer to a reproducibility of ~$10^{-3}$ deg.

Two fills of $CO_2$ were used, each of nominal purity better than 99.99%. The critical temperatures were measured to be $T_c = 30.99 \pm 0.01$°C using the platinum resistance thermometer which

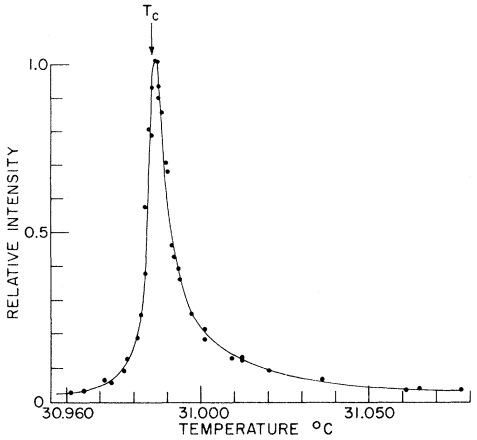


FIG. 1. Dependence of scattered intensity on temperature.

had been calibrated at the National Bureau of Standards.

Figure 1 shows the temperature dependence of scattered intensity at 13.5° for one sample of $CO_2$ for temperatures close to $T_c$. Within a few millidegrees of $T_c$ the scattered intensity varied markedly over the height of the cell[1,2] owing to the variation in density caused by compression of the fluid under its own weight. The intensities plotted for $T > T_c$ were maxima obtained close to the center of the cell. Below $T_c$ the intensities plotted were maxima obtained at heights $\lesssim 0.5$ mm above or below the meniscus.

Some of the main features of the data are evident in Fig. 1: the greater scattered intensity for a given $\Delta T$ above than below $T_c$ and the sharp intensity peak near $T_c$. The peak intensity was found also to coincide with the minimum Rayleigh linewidth.[1,2]

In Fig. 2 the data are plotted logarithmically to exhibit the power-law dependence of the scattering as a function of the temperature distance from $T_c$. Data obtained both above and below the critical temperature for two scattering angles and for both samples of carbon dioxide are included on this plot. (For clarity, the liquid-case data are omitted; scattering from the liquid was typically 15% greater than from gas at the same temperature.[1]

The temperature $T_c$ was chosen to be that temperature for which the ratio of temperature distances $\Delta T$, $\Delta T'$ for equal scattered intensities above and below the critical temperature remained most nearly constant. The precision of this definition was a few tenths of a millidegree. The temperature $T_c$ found in this way for one

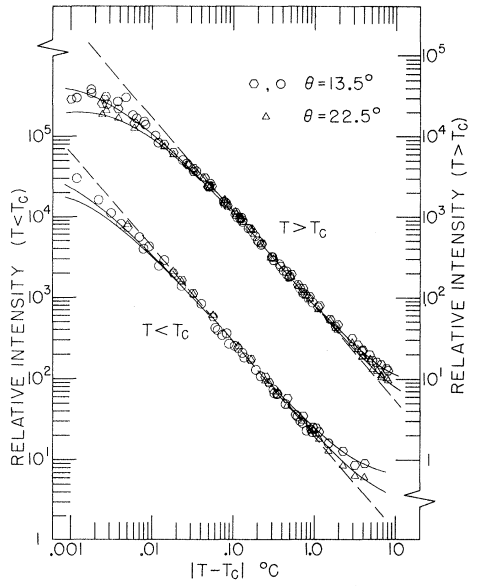


FIG. 2. Intensity of light scattered through angles of 13.5 and 22.5° (a) above and (b) below the critical temperature. Dashed lines represent ideal, isotropic scattering from an infinitely thin layer of $CO_2$. Solid lines show the result of including corrections for anisotropy, extinction, and background. The upper solid line of each pair at each temperature is for 13.5° scattering, the lower for 22.5° scattering.

sample is shown in Fig. 1. The value $T_c$ found for each sample agreed within $10^{-3}$ deg with the temperature for which the intensity of the scattered light was maximum and for which the width of the Rayleigh line was minimum. It agreed within a few millidegrees with the temperature at which there first appeared a meniscus, as observed visually. (It was felt that appearance of a meniscus provided an imprecise definition of the critical temperature because large gradients of density slightly above $T_c$ were difficult to distinguish visually from the abrupt discontinuity of density at $T_c$.)

Intensities shown in the lower portions of Fig. 2 were first corrected for a small, constant background intensity. Corrected data are represented by the dashed lines; the solid lines correspond to the dashed lines without the corrections and show goodness of fit to the data which have been plotted in Fig. 2 without applying corrections.

From the corrected intensities, absolute compressibilities were calculated for $0.1 < |\Delta T| < 10$ deg, employing Einstein's equation [see Giglio and Benedek,[3] Eq. (1)], the Lorentz-Lorenz relation, and the value[4] $n_c = 1.106$ for the critical index of refraction. The compressibilities thus ob-

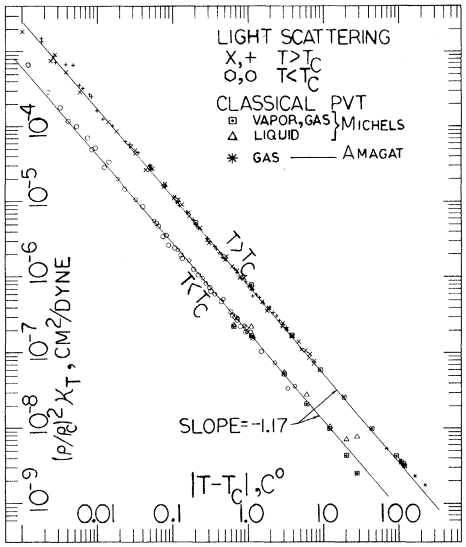


FIG. 3. Temperature dependence of the compressibility of carbon dioxide. Classical data, plotted for $T_c$ = 31.00°C, are from Refs. 7 and 8.

tained are shown in the middle portion of Fig. 3.

Intensities obtained closer than 0.1 deg from $T_c$ required corrections for anisotropy and extinction.

The corrections for extinction were made on the assumption that the compressibility obeys the same power law close to $T_c$ that was found for temperature distances >0.1 deg from $T_c$. The calculations used Einstein's extinction expression as modified by Ornstein and Zernike (OZ) [see Puglielli and Ford,[5] Eq. (2)].

The corrections for anisotropy were made on the assumption that the scattering obeys OZ theory, with a correlation length above $T_c$ of the form $\xi = 63(T-T_c)^{-0.59}$ where $\xi$ is in Å and $T-T_c$ is in °C. Below $T_c$ it was assumed the correlation length is smaller at each $\Delta T'$ in proportion to the square root of the ratio of compressibilities for $|\Delta T'| = \Delta T$. (Our expression for the correlation length above $T_c$ agrees reasonably well with x-ray data of Chu[6] obtained for $\Delta T$ ~ 1 deg and with our data[1,2] for light scattering ~10 mdeg above $T_c$. The exponent $\nu = 0.59$ is smaller than Chu's 0.67, but the agreement of $\xi$ itself with Chu's data is nearly within error bars.[2])

In Fig. 2, the dashed lines close to $T_c$ represent the scattering which would be expected for an infinitesimal layer of $CO_2$ from OZ theory, upon extrapolation to zero scattering angle, if the compressibility continues to obey the simple power law shown in the middle of Fig. 3. The solid lines include corrections for anisotropy and extinction. For $|\Delta T| > 10$ mdeg and the small scattering angles used in this experiment, the anisotropy of the scattering contributed principally through its effect on extinction. For example, at $\Delta T = 10$ mdeg, the extinction in our cell—5 mm path length—was calculated to be 35% including anisotropy (OZ theory), but would have been 60% ignoring anisotropy (unmodified Einstein theory).

Although they represent the data better than the dashed lines, the solid lines in Fig. 2 do not agree perfectly with the data obtained close to $T_c$. This may be partly because no correction has been made for multiple scattering. Multiple scattering close to $T_c$ results in larger intensities than indicated by the solid lines. (It is readily calculated that the dominance of forward scattering predicted by OZ theory means that an appreciable fraction of the "extinguished" light—e.g., several percent for $\Delta T \sim 3$ mdeg—is still available for scattering, and accompanies singly scattered light into the photodetector.) Another effect not corrected for is the averaging of the incident light beam over noncritical densities very near $T_c$, where the density gradients become especially steep.[1,2] The data obtained close to $T_c$ also contain especially large errors because of uncertainty (~0.3 mdeg?) in the precise value of $T_c$ and inaccuracies in controlling and measuring temperature intervals. (We have been unable to demonstrate to our satisfaction that we measured temperature distances reproducibly to an accuracy better than 1 mdeg.) Thus the reasonably good agreement between the solid lines in Fig. 2 and the observed scattered intensities within 5 mdeg of $T_c$ may be fortuitous.

The compressibilities derived from all supercritical and vapor-phase data obtained at 13.5° scattering angle are shown in Fig. 3, together with values for the compressibility derived from classical measurements of the pressure and volume of $CO_2$ as a function of temperature.[7,8] It appears that along the critical isochore over approximately five decades in temperature distance above $T_c$ all of the available data agree with a compressibility $\kappa_T = (7.8 \pm 0.5) \times 10^{-7}(T - T_c)^{-\gamma}$ cm²/dyn, with $\gamma = 1.17$. Along both sides of the coexistence curve over approximately four decades of temperature distance below $T_c$, it appears that $(\rho/\rho_c)^2 \kappa_T = (1.9 \pm 0.2) \times 10^{-7}(T - T_c)^{-\gamma'}$ cm²/dyn for the vapor phase, with $\gamma' = 1.17$. (Below $T_c$, the value for liquid was typically 15% higher than for gas at the same temperature.

The light-scattering data were not sufficiently accurate to determine what fraction of the dissymmetry between liquid and gas to ascribe to the difference in index of refraction.[4] In our analysis we always took $n = n_c$.) The dimensionless compressibilities quoted in the abstract are obtained on multiplying by $P_c = 73$ atm and converting to $t = (T - T_c)/T_c$, with $T_c = 304$°K.

Although somewhat larger values for $\gamma$ and $\gamma'$ have been reported in the literature,[9] our data appear to be inconsistent with values for these exponents outside the limits $\gamma = 1.17 \pm 0.03 = \gamma'$.[10] Our data do not rule out the possibility of a larger exponent for temperatures closer than 0.03 deg from $T_c$. But, since the correlation length is by then much greater than the range of ordinary intermolecular forces while still small compared to the dimensions of our apparatus, we have preferred to assume a single exponent for the entire range of temperature, an assumption which we also believe to be consistent with our data. (That compressibilities more than 100 deg above $T_c$ or 20 deg below should cease to follow a simple power law is not surprising, as the long-range correlation length $\xi$ has by then decreased to ~4 Å, which is comparable to intermolecular spacings and the direct correlation range.[2])

The difference in the magnitude of $\kappa_T$ for equal-temperature distances above and below $T_c$, combined with the equality $\gamma = \gamma'$ for the exponents, suggests that the compressibility is homogeneous of degree $\gamma$ in $|T - T_c|$ and $|\rho - \rho_c|^{1/\beta}$, where $\beta$ is the degree of the coexistence curve. Along the critical isotherm the compressibility then varies as $|\rho - \rho_c|^{\delta - 1}$, with $\delta - 1 = \gamma/\beta$. For $\gamma = 1.17$ and[9] $\beta = 0.35$ this gives for the degree of the critical isotherm $\delta = 4.35$, in reasonably good agreement with $PVT$ measurements.[9,11] (Results of light-scattering measurements made along the critical isotherm[1] will be published elsewhere.[2])

The exponent $\gamma = 1.17$ substituted into the scaling-law relation[12] $\gamma + 2\beta + \alpha = 2$ with $\beta = 0.35$ yields $\alpha = 0.13$, in good agreement with the value $0.12 \pm 0.01$ found for this exponent in recent measurements of the specific heat of $CO_2$ at constant volume.[13] The exponent $\alpha = 0.13$ subtracted from $\gamma$ yields a prediction $\gamma - \alpha = 1.04$ for the Landau-Placzek ratio for $CO_2$, to be compared with the experimental values for this ratio of[14] $0.95 \pm 0.15$ and[15] $1.02 \pm 0.03$. Our value for $\gamma$ and our choice $\nu = 0.59$ are consistent with Fisher's relation[16] $\gamma = (2 - \eta)\nu$ with $\eta = 0$, as required for the complete validity of OZ theory used in analyzing our data. Our choice for $\nu$ agrees reasonably well with the value found for xenon by Giglio and Benedek[3] and the value $\nu = 0.62 \pm 0.02$ derived recently by Sengers[17] from an analysis of Rayleigh linewidths[18] for $CO_2$. (We have independently obtained Rayleigh linewidths[1,2] which agree within error bars with those published in Ref. 18.)

To our knowledge, this is the first time such extensive agreement has been found between scaling-law and thermodynamic predictions and measured exponents.

---

*Research supported by the National Science Foundation.

[1]B. S. Maccabee, thesis, The American University, 1970 (unpublished).

[2]B. S. Maccabee and J. A. White, to be published.

[3]M. Giglio and G. B. Benedek, Phys. Rev. Lett. 23, 1145 (1969).

[4]J. M. H. Levelt Sengers, J. Straub, and M. Vicentini-Missoni, to be published.

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

[6]B. Chu, J. S. Lin, and J. A. Duisman, Phys. Lett. 32A, 95 (1970).

[7]A. Michels, B. Blaisse, and C. Michels, Proc. Roy. Soc., Ser. A 160, 358 (1937); A. Michels, C. Michels, and H. Wouters, Proc. Roy. Soc., Ser. A 153, 214 (1935).

[8]*International Critical Tables* (McGraw-Hill, New York, 1929), Vol. 3, p. 12.

[9]M. Vicentini-Missoni, J. M. H. Levelt Sengers, and M. S. Green, J. Res. Nat. Bur. Stand., Sect. A 73, 563 (1969), and Phys. Rev. Lett. 22, 389 (1969).

[10]The fit of the scaled equation of state (Ref. 9) to the Michels $CO_2$ data was repeated for the choice $\gamma = 1.17$, $\delta = 4.35$. To obtain an optimum fit, the value of $T_c$ had to be increased to 31.03°C instead of $30.96 \pm 0.04$°C of Ref. 9. The quality of the fit was not as good as that of Ref. 9; the standard deviation was about 20% higher and systematic deviations from the fit were present. (J. M. H. Levelt Sengers, private communication.)

[11]J. Straub, Phys. Lett. 31A, 453 (1970).

[12]B. Widom, J. Chem. Phys. 43, 3898 (1965).

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

[14]R. W. Gammon, H. L. Swinney, and H. Z. Cummins, Phys. Rev. Lett. 19, 1467 (1967).

[15]N. C. Ford, Jr., K. H. Langley, and V. G. Puglielli, Phys. Rev. Lett. 21, 9 (1968).

[16]M. E. Fisher, J. Math Phys. 5, 944 (1964).

[17]J. V. Sengers and P. H. Keyes, Phys. Rev. Lett. 26, 70 (1971).

[18]H. L. Swinney and H. Z. Cummins, Phys. Rev. 171, 152 (1968).