Experimental investigation of gravitationally induced effects in dynamical critical-point theories

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The authors have experimentally examined the height dependence of the Rayleigh linewidth in CO_2 at $T - T_c = 0.001\,^\circ C$. The results are compared with the predictions of the mode-mode coupling, decoupled mode, and dynamic-droplet theories of the critical point. Linewidth data are more easily described by the decoupled-mode theory than by other models.

INTRODUCTION

As a simple fluid approaches its critical point, there is a divergence in the isothermal compressibility (K_T). In turn, the diverging compressibility gives rise to an increase in the correlation length, and a consequent narrowing of the Rayleigh linewidth (Γ) of light scattered from the critical system. In addition, the fluid becomes so compressible that gravitational forces induce an appreciable vertical density gradient. Only that part of the fluid located at the correct sample height (Z_c) is actually at the critical density. Consequently, experiments conducted close to the critical point must take into account the vertical density gradient and the concomitant height dependence of the Rayleigh linewidth. Following the suggestion of Kim *et al.*,[1] we can utilize the height dependence of the Rayleigh linewidth as a sensitive test of the dynamic theories of the critical point. The temperature dependence of the Rayleigh linewidth near the critical point has been described in three theoretical models[2]: the mode-mode coupling,[3-6] decoupled-mode,[7,8] and dynamic-droplet theories.[9-12] By using the parametric representation of the equation of state, Kim *et al.*[1] and Leung and Miller[13] have derived the height dependence of the Rayleigh linewidth in the mode-mode coupling and decoupled-mode theories. Their analyses can be readily applied to the dynamic-droplet model as well. We report a rather extensive experimental measurement of the Rayleigh linewidth as a function of sample height in CO_2 at $T - T_c = 0.001\ ^\circ C$. The results are compared explicity with the three existing theoretical models.

THEORY

First, we summarize the three existing theories. In both mode-mode coupling (MMC) and decoupled-mode (DCM) theories the Rayleigh linewidth Γ is assumed to be the sum of a critical and background part: $\Gamma = \Gamma^C + \Gamma^B$.[2] In MMC Γ^C reads[3-6]

$$\Gamma^C_{\mathrm{MMC}} = k_B T C(q\xi) K_0(q\xi) R(q\xi)/6\pi\eta_S \xi^3 , \qquad (1)$$

where k_B is Boltzmann's constant, T the temperature, and ξ the correlation length. The magnitude of the scattering wave vector $q = (4\pi/\lambda)\sin\frac{1}{2}\theta$ is given in terms of the incident wavelength λ in the medium and the scattering angle θ. $R(q\xi)$ and $C(q\xi)$ are numerically determined factors,[5,14] and $K_0(q\xi)$ is given by

$$K_0(q\xi) = \tfrac{3}{4}\{1 + (q\xi)^2 + [(q\xi)^3 - 1/q\xi]\ \arctan(q\xi)\} . \qquad (2)$$

The shear viscosity η_S is given by

$$\eta_S = \eta_S^B + (8\bar{\eta}/15\pi^2)\ln q_D\xi , \qquad (3)$$

where η_S^B is the background part of the shear viscosity, extrapolated from data taken away from the critical point, and $\bar{\eta}$ and q_D are parameters obtained by a fit to the experimental viscosity data.[2]

The decoupled-mode expression for the critical part of the linewidth is[7,8]

$$\Gamma^C_{\mathrm{DCM}} = k_B T K_0(q\xi) C(q\xi)/6\pi\eta_S^{\mathrm{eff}}\xi^3 , \qquad (4)$$

where

$$\eta_S^{\mathrm{eff}} = \eta_S^B + \frac{8\bar{\eta}}{15\pi^2}[\ln q_D\xi - \tfrac{1}{2}\ln(1 + q^2\xi^2) + \tau(q\xi)] , \qquad (5)$$

and $\tau(q\xi)$ is a numerically determined factor.[2]

The background part of the linewidth is the same for the MMC and DCM theories. It is only weakly density dependent, and is at most a few percent of the total linewidth near the critical point. Its value is

$$\Gamma^B = \lambda^B q^2(1 + q^2\xi^2)/\rho c_p , \qquad (6)$$

where λ^B denotes the background thermal conductivity, extrapolated from the data taken away from the critical point, ρ the density, and c_p the specific heat at constant pressure.[2]

In the dynamic-droplet (DD) theory, the field-field correlation function of the Rayleigh scattered light is a sum of exponentials rather than a single exponential. Thus, DD predicts a non-Lorentzian shape for the Rayleigh linewidth, in disagreement with experiment.[15] The decay rate reads

$$\Gamma_{DD} = \gamma (k_B T / 6\pi\eta_S^B) q^2 (\xi^{-2} + q^2)^{1/2} . \quad (7)$$

Here γ is a factor of order 1 which reflects the predicted non-Lorentzian behavior of the Rayleigh line.

Each of the theories expresses the Rayleigh linewidth as a function of the correlation length ξ. Kim *et al.* relate the correlation length to the density using the linear parametric equation of state of Schofield, Lister, and Ho.[16–18] This equation of state has been shown to describe experimental PVT data to high accuracy for a number of fluids.[19,20] The height dependence of the density is calculated from the equation of state and the relation

$$Z - Z_c = (1/g)[\mu(\rho, T) - \mu(\rho_c, T)] , \quad (8)$$

where g is the acceleration of gravity, μ is the chemical potential, and Z_c is the height corresponding to the critical density. This leads to a height dependence of the correlation length, which is applied to the three theories. The results of Kim *et al.*[1] and of Leung and Miller[13] for the height dependence of Γ are in substantial agreement with one another, even though they employ somewhat different equations of state. The DD result presented in Fig. 3 was derived using only the linear parametric equation of state employed by Kim *et al.*

Recently, Siggia *et al.*[21] have used renormalization-group methods to estimate a correction factor to the simplest approximation of the MMC theory. They find

$$D_{RG} = \Gamma / q^2 = 1.2 D'_{MMC} , \quad (9)$$

where D'_{MMC} is the diffusion coefficient calculated by the simplest version of the MMC theory, i.e., the MMC theory without the viscosity, vertex, and correlation-function corrections. Swinney and Henry have demonstrated that the inclusion of these three corrections results in a temperature-dependent correction factor which varies from 1.1 to 1.3 near the critical point. Thus there is an approximate equivalence between the renormalization-group correction to the simple MMC theory, and the corrections due to the viscosity, vertex, and correlation-function modifications. In our calculation we have adopted the MMC theory as presented by Swinney and Henry.[2,22]

EXPERIMENT

The experimental procedure was as follows: A sample of 99.95%-pure CO_2 was confined at the critical density in a sealed quartz cell of internal dimensions 2 cm × 0.5 cm × 0.5 cm. The time constant for equilibriation in the formation of gravitationally induced gradients, τ, has been shown to be a function of the height of the cell. Giglio and Vendramini have observed that τ is given by $\tau = a^2/\pi^2 D$, where a is the sample height and D the diffusion coefficient.[23] Thus, a CO_2 cell of height 2 cm has a time constant for the formation of gravitationally induced gradients of approximately 12 h at $T - T_c = 10^{-3}$ °C. In our experiment, the fluid was allowed 36 h to reach equilibrium following a temperature change. The cell was translated vertically in order to scan Γ as a function of height. Since movement also disturbs the density profile, the fluid was allowed a similar time interval to reach equilibrium each time the cell was translated.

The cell was mounted in a temperature-controlled oil bath. Two temperature sensors were used in the controller, a thermistor and a Hewlett-Packard 2801A quartz thermometer. The quartz thermometer was observed to have less long-term drift (over periods of weeks to months) than the thermistor, and it was used exclusively for the balance of the experiment. The temperature corresponding to each linewidth measurement was determined with a platinum resistance thermometer, which was also mounted in the bath. The platinum resistance thermometer revealed that the controller was subject to long-term drifts of the set point of approximately 1×10^{-3} °C/week. The set point of the controller was readjusted at intervals to compensate for this drift.

The temperature-control electronics were similar in design to that described by Sarid and Cannell,[24] and were mounted in an insulated box, which was maintained at constant temperature to within ±1 °C. Temperature gradients in the bath were measured using the quartz thermometer, and were restricted by stirring to less than 10^{-4} °C throughout the volume of the bath. The temperature of the oil bath was found to be stable to 10^{-4} °C over periods of days.

A vertically polarized laser beam ($\lambda_0 = 457.9$ nm) was incident on the cell and focused to a diameter of approximately 50 μm. The scattered light was collected at a 90° scattering angle and detected by an ITT FW130 photomultiplier (Fig. 1). At this scattering angle and beam diameter, averaging of Γ due to the vertical density gradient is negligible.[1] The phototube signal was fed to a 61-channel, single-clipped digital autocorrelator and analyzed according to the prescription of Jakeman *et al.*[25]

Sorenson *et al.* have measured the effect of local laser heating in critical fluids by monitoring the time dependence of the low-angle scattering intensity. They observed that the scattered intensity decreased exponentially with time, eventually

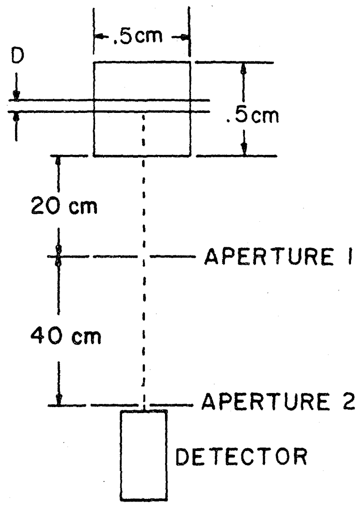

FIG. 1. Top view of the light-scattering cell. The laser-beam diameter was $D=50$ μm. The diameter of aperture 2 was 100 μm, and the diameter of aperture 1 was varied between 100 and 200 μm.

reaching a constant value. In methanol-cyclohexane, the heating effect was as much as 2×10^{-3} °C/mW of incident radiation.[26,27] This suggests that heating effects could potentially affect our linewidth measurements. In our measurement, the dependence of the scattering intensity and linewidth on local temperature changes can be estimated as follows. Consider the Ornstein-Zernike expression for the intensity of light scattered from a critical fluid:

$$I=A/(q^2+\xi^2)\,, \tag{10}$$

where A is not strongly temperature dependent. This leads to a temperature dependence of the scattered intensity of approximately 1%/m °C at a 90° scattering angle. The local heating effect on the linewidth can also be estimated, using, for instance, the dynamic-droplet theory:

$$\Gamma=A'q^2(\xi^{-2}+q^2)^{1/2}\,. \tag{11}$$

Again at a 90° scattering angle, Eq. (10) leads to a temperature dependence of 0.6%/m °C. This is well within the scatter in our data (2%). In our experiment, no time-dependent intensity or linewidth changes were observed below an input power level of 0.5 mW. In the power range of 2–10 mW, the linewidth was observed to change with time, reaching equilibrium in a period of 30 min to 2 h. All measurements of Γ were performed below the 0.5-mW power level, where the local-heating contribution to Γ is much smaller than the error in the linewidth measurement.

The critical temperature was determined to within 10^{-4} °C by the visual observation method

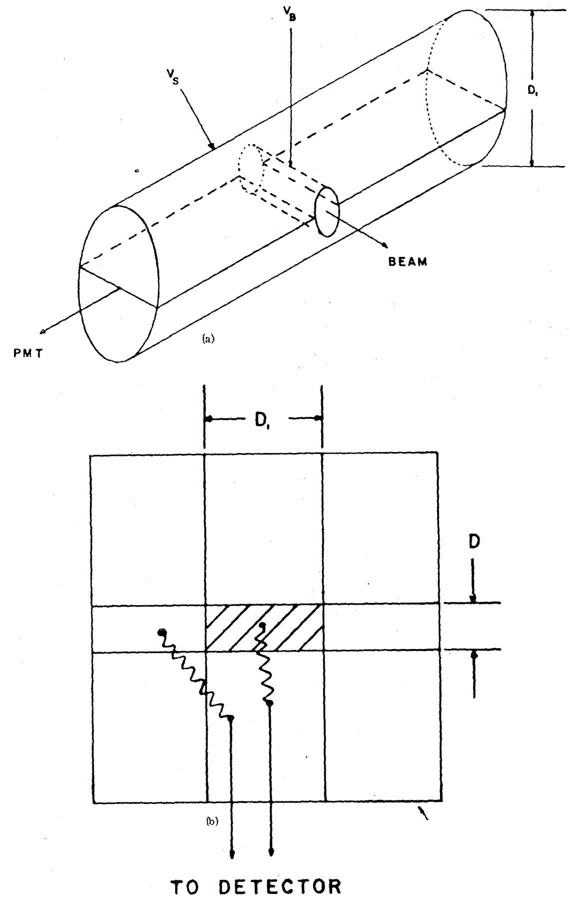

FIG. 2. (a) Volume V_s seen by the PMT detector. The laser beam passes through the volume V_B. The laser-beam diameter is $D=50$ μm. The diameter of V_s is D_1 $=450$ μm for the 200-μm aperture and $D_1=275$ μm for the 100-μm aperture. (b) Top view of the light-scattering cell, illustrating two possible second-order scattering events. V_B is the crosshatched area.

described by Moldover.[28] This method requires that the laser beam be incident on the fluid for observation purposes only. During the approximately 1-min observation time, local-heating effects do not manifest themselves. The height corresponding to the critical density was determined from measurements of linewidth as a function of height at $T-T_c=0.018$, 0.010, and 0.006 °C and was found to be independent of temperature.

The effect of multiple scattering on our measurement of the decay rate Γ was investigated as follows. A Glan-Thompson polarizer with an extinction ratio of 5×10^{-6} was placed between the sample and the photodetector and adjusted to pass only the vertical component of the scattered light. The measured Γ values were found to be unaffected by the removal of the polarizer. This clearly shows that depolarized multiple scattering does not affect our values, although the depolarized intensity was approximately 2% of the total measured intensity. Recent theoretical results suggest that the total (i.e., polarized and depolarized) double-scattered intensity might contribute 10% or more to the scattered intensity near the critical point.[26,29] In order to assess the effect of this total multiple scattering on our linewidth measurement, we measured Γ using two different collection-aperture diameters, i.e., 200 and 100 μm.

The scattering volume V_s as observed by the photodetector was approximately a cylinder of revolution of diameter D_1, determined by the two collection-aperture sizes, and their distances from the sample cell [Figs. 1 and 2(a)]. The collection system was arranged so that the primary beam passed through the center of and was perpendicular to the axis of the scattering volume [Fig. 2(a)]. The single-scattered component of the scattered light originates from the volume V_B of the primary beam. The single-scattered light emanating from the entire beam volume in the fluid can undergo one or more scattering events from secondary or higher-order scattering centers within V_s [Fig. 2(b)]. Increasing the collection-aperture radius from 100 to 200 μm enlarges V_B by a factor of 2, while the multiple-scattering volume V_s increases by a factor of approximately 4.[30] This suggests that multiple scattering should make an approximately two fold-greater contribution to the total scattered light with the larger collection aperture than with the smaller. Thus, if multiple scattering affects the linewidth, the linewidth would be expected to be a function of aperture diameter. However, the paired "t" test revealed that there is no statistically significant difference in the linewidth data for the two collection systems at the 99.5% confidence level. This indicates that the effect of multiple scattering on our linewidth data is less than $\pm 1\%$.

In addition, a Koppel cumulant analysis[31] of the data gave $K_2/K_1^2 = 1.9\times10^{-2} \pm 5\times10^{-2}$ for the larger aperture and $K_2/K_1^2 = 2.3\times10^{-2} \pm 3\times10^{-2}$ for the smaller aperture. Since K_2/K_1^2 is a measure of the departure from single-exponential behavior, and is expected to be large (i.e., $K_2/K_1^2 > 0.1$) for the case of multiple scattering,[15,26,31] cumulant analysis provides additional evidence that multiple scattering must make a small contribution to the total linewidth.

It is not so far clearly understood in the literature why multiple scattering does not affect the measured Γ values. Sorensen *et al.*[26] proposed that the double- (Γ_D) and single- (Γ_S) scattered decay rates are more or less equal. We feel that a more rigorous analysis for Γ_D is in order before a clear conclusion can be drawn. Additionally, it should be noted that the linewidths do not strictly add according to the ratio of their intensities I_D/I_S, but rather as the ratio of the product of the intensities with the corresponding signal to background ratio, i.e., $g_2(0)/g_2(\infty)$. If $g_2(0)/g_2(\infty)$ is much smaller for double than for single scattering, then double scattering would make a small contribution to the total linewidth.

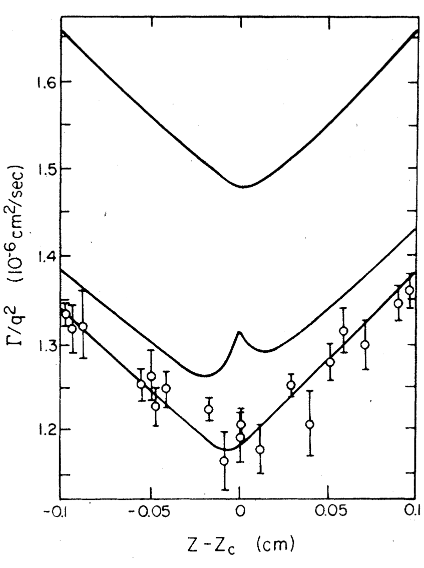

FIG. 3. Scaled Rayleigh linewidth as a function of height for CO_2 at $T - T_c = 0.001\,°C$. The upper curve is the prediction of the dynamic-droplet theory with $\gamma = 1$. The middle curve is the mode-mode coupling result, and the lower curve is the prediction of the decoupled-mode theory. The uncertainty in the height of the data points is ± 0.005 cm.

RESULTS

We now present the measured decay rate as a function of height at $T - T_c = 0.001\,°C$ (Fig. 3). In Fig. 3 the lower two curves are the results of Kim *et al.* for the mode-mode coupling and decoupled-mode theories, and the upper curve is the dynamic-droplet result for $\gamma = 1$. The rms deviation of the measured points from the decoupled-mode theory is 2.73%, a value comparable to the intrinsic scatter of the data. The rms deviations from the mode-mode coupling and dynamic-droplet results are 7.95% and 33.95%, respectively. We note that the dynamic-droplet theory can be forced to fit our results if γ in Eq. (7) is treated as a free parameter. In this case, a value of $\gamma = 0.80$ results in a fit of rms deviation of 2.24%. It must be noted that γ is a parameter arising from the DD prediction of a nonexponential correlation function. This prediction has been shown to be incorrect.[15] Further, Ackerson *et al.* have estimated γ to lie in the range $0.88 \leq \gamma \leq 1.25$, the limits corresponding to the correlation function slope at the $1/e$ point and near zero, respectively.[9] Experimentally, Sorenson *et al.* have found $\gamma = 1.16$ for the system carbon tetrachloride-perfluoromethylcyclohexane,[10] and $\gamma = 1.03$ for the system 3-methylpentane-nitroethane.[25] If γ is restricted to lie in the range $0.88 \leq \gamma \leq 1.25$, the minimum rms deviation is 14.04%, corresponding to $\gamma = 0.88$.

In conclusion, our results for the height dependence of the Rayleigh linewidth in CO_2 are most easily described by the decoupled-mode theory, though the dynamic-droplet theory can be forced to fit if γ is treated as a free parameter. There is no evidence of the "kink" near the critical height predicted by the mode-mode coupling theory.[1,13]

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