Scattering of Sound by Sound in the Vicinity of the Liquid-Vapor Critical Point

N. Mujica, R. Wunenburger, and S. Fauve

Laboratoire de Physique Statistique, Ecole Normale Supérieure, UMR 8550, 24, rue Lhomond, 75 005 Paris, France

(Received 5 November 2002; published 12 June 2003)

We report an experimental study of the scattering of sound by sound in the vicinity of the liquid-vapor critical point of carbon dioxide. We measure the amplitude of the scattered difference frequency wave generated by acoustic bulk nonlinearities. We observe that it is strongly increased in the vicinity of the critical point.

DOI: 10.1103/PhysRevLett.90.234301 PACS numbers: 43.25.+y, 05.70.Jk, 62.60.+v

Introduction.—The study of physical properties of fluids in the vicinity of their liquid-vapor critical point (CP) has a long history that has witnessed several revivals of interest motivated by fundamental questions such as the study of critical phenomena and their universal behavior [1,2], phase transition dynamics [3], and also by applications of supercritical fluids to various chemical engineering problems [4]. Acoustic techniques have been widely used to probe fluids in the vicinity of their CP. Low frequency sound velocity is directly related to the singular behavior of thermodynamic properties [5–8] while sound absorption gives information about transport properties and critical relaxation processes [9–12]. Both absorption and dispersion are strongly affected by critical fluctuations and many theoretical studies have been devoted to elucidate the relevant coupling mechanisms responsible for the anomalous critical absorption and dispersion [13–17]. Most of the experiments on acoustics in critical fluids have been performed in the linear regime so far, except an observation of rarefaction shock waves that has been related to an anomalous increase of sound velocity with decreasing pressure at constant entropy close to the CP [18]. The possibility of a slow divergence of the nonlinear acoustic parameter along the critical isochore has also been discussed in the literature [18]. We report here the experimental observation that the nonlinear acoustic behavior of a fluid is strongly enhanced in the vicinity of the CP.

Experimental setup and measurement techniques.—Experiments are performed in a stainless steel cylinder, $D = 200$ mm in inner diameter and $H = 100$ mm in height sketched in Fig. 1, immersed in a thermally regulated water bath of volume 250 l.

The vessel is filled with carbon dioxide at nearly critical density. This is roughly achieved by visual inspection of the liquid-vapor meniscus using two opposite windows made of sapphire. The pressure within the vessel is measured with a resistive transducer (Entran EPXM-N02-100B) and temperature is measured with two platinum resistors. The first one is located along the axis of the cylinder, 60 mm above the bottom, i.e., just below the acoustic scattering volume. The second one is along the lateral boundary, 25 mm below the top.

The pressure-temperature curve is recorded during each experiment in order to determine the filling density. This is done by comparing the variation of its slope from the two-phase to the supercritical state with the prediction given by a standard state equation [19]. Three different fluid densities ρ are thus determined: $\rho/\rho_c = 0.905, 0.95$, and 0.97 ± 0.005, where ρ_c is the critical density.

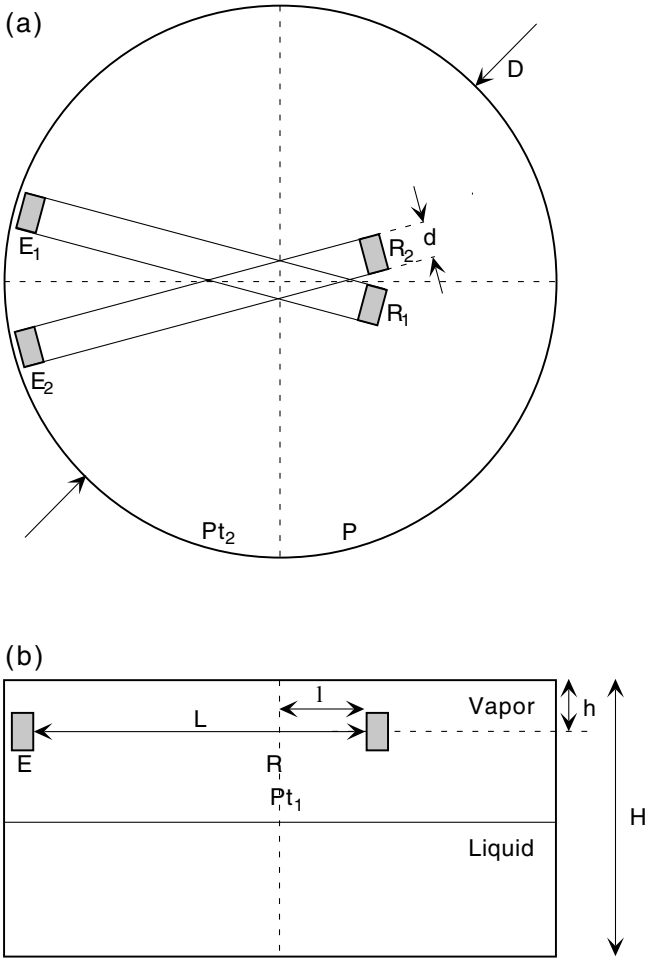

FIG. 1. Sketch of the experimental setup. (a) Top view, (b) side view. E_i: sound emitters, R_i: sound receivers, Pt_i: platinum resistors, P: pressure transducer. $D = 200$ mm, $L = 107$ mm, $l = 30$ mm, $H = 100$ mm, and $h = 25$ mm.

Four piezoelectric transducers are located in the plane perpendicular to the cylinder axis, 75 mm above its bottom. Two of them, 30° apart along the inner lateral boundary, (E_1 and E_2 in Fig. 1) are used as emitters. Two acoustic sinusoidal waves, at frequencies $f_1 = 107$ kHz and $f_2 = 203$ kHz, are generated toward the center of the cell where they interact nonlinearly. The emitters diameter, $d = 20$ mm, gives the typical size of the scattering volume. The diameter of the vessel has been chosen large enough in order to avoid near field effects of the emitters. The two other piezoelectric transducers are used as receivers (R_1 and R_2 in Fig. 1). They are located at a distance L from each emitter. For the measurements reported below, $L = 107$ mm, but comparison with measurements performed for $L = 160$ mm has been used in order to determine the absolute value of sound absorption as a function of temperature.

The two received wave pressure amplitudes, P_1 and P_2, and their phases, ϕ_1 and ϕ_2, are measured by lock-in amplifiers (Stanford SR844RF and SR830RF). Each measurement is averaged during 1 min. The amplitude P_m of the nonlinearly generated wave at frequency $f_2 - f_1 = 96$ kHz, recorded by the transducer R_1, is measured with a spectrum analyzer (Agilent 3589A) after averaging during 1 min on a 78 Hz frequency band. During the experiments, the two calibrated temperature probes far apart display temperature differences smaller than 20 mK. The experiments are conducted as follows: we start with the water bath at about 2° above the critical temperature ($T_c = 304.13$ K) and we turn off the temperature regulation. The bath being well insulated, the temperature of the vessel begins to decrease slowly, roughly at a rate 1 mK per minute. We take measurements every 1 min and average them during 1 min. Thus, we record the temperature, the static pressure, the two acoustic wave's amplitudes P_i and their phases ϕ_i and the difference frequency wave amplitude P_m, roughly every 2 mK. As said above, the size of the vessel has been determined to avoid near field effects. Thus, it is larger than in usual CP experiments and density gradients which involve very long relaxation times and the effect of gravity are important close to the CP [20]. However, the paths followed by the acoustic waves and the scattering region involve only a small horizontal layer within the vessel. Moreover, our aim is not to perform quantitative measurements of critical exponents but to show the increase of acoustical nonlinearities close to the CP. Fortunately, it has not been necessary to go very close to the CP to display this effect, already visible a few tenths of a Kelvin from the CP.

Experimental results.—We first present our data related to sound velocity and absorption versus temperature in order to check agreement with previous experimental measurements close to the CP. Sound velocity c can be obtained from the phase difference, $\Delta\phi_i = -\omega_i L/c$, where $\omega_i = 2\pi f_i$ is the wave pulsation ($i = 1, 2$) and L is the distance between the emitter and the corresponding receiver. The lock-in amplifiers only measure ϕ_i, the phases of the received signals. In order to avoid the determination of the absolute value of the unwrapped phases, we compute $d\phi_i/dT$ from the experimental measurements and compare with $\omega_i L c^{-2} dc/dT$ where $c(T)$ is determined by using a standard state equation of carbon dioxide [21]. Figure 2 shows that the agreement is good. We note that for one series of experiments ($\rho/\rho_c = 0.97$), we had to shift the temperature origin by 160 mK in order to get a good agreement. We think that this may result from nonrelaxed gradients within the vessel.

Measurements of the pressure wave amplitudes, P_1 and P_2, as a function of temperature show that the waves are strongly attenuated in the vicinity of the CP, roughly by 3 orders of magnitude at 0.1 K from T_c. Note that for the two larger filling densities, this absorption does not allow one to perform measurements in the very-critical region of each sample, the signal to noise ratio being too small. Using the measurements performed for $L = 107$ mm together with additional ones for $L = 160$ mm, we can estimate the absorption coefficients per wavelength $\alpha_1\lambda$ (respectively, $\alpha_2\lambda$) at frequency f_1 (respectively, f_2). They are displayed in Fig. 3 for both the vapor and the supercritical phases of the most absorbing sample ($\rho/\rho_c = 0.97$).

We now consider the generation of the wave at frequency $f_2 - f_1$ as a function of temperature. This wave is created by nonlinearities of the conservation equations and of the state equation. For two waves of amplitudes A_1 and A_2, propagating along a distance L_{int} in the same direction in a medium without dissipation, the amplitude A_m of the difference frequency wave is given by

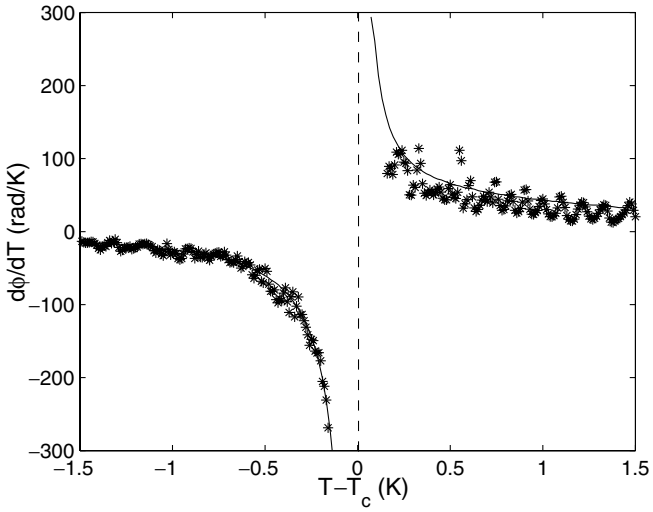

FIG. 2. Temperature derivative $d\phi/dT$ of the phase of the measured wave at frequency $f_1 = 107$ kHz with respect to the temperature T (*). $d\phi/dT = \omega_1 L c^{-2} dc/dT$, calculated from a standard state equation [21], as a function of T (solid line). The density is $\rho \approx 0.97\rho_c$, $L = 107$ mm. The minimum value of sound velocity in our experiments is 143 m/s (see Ref. [21]).

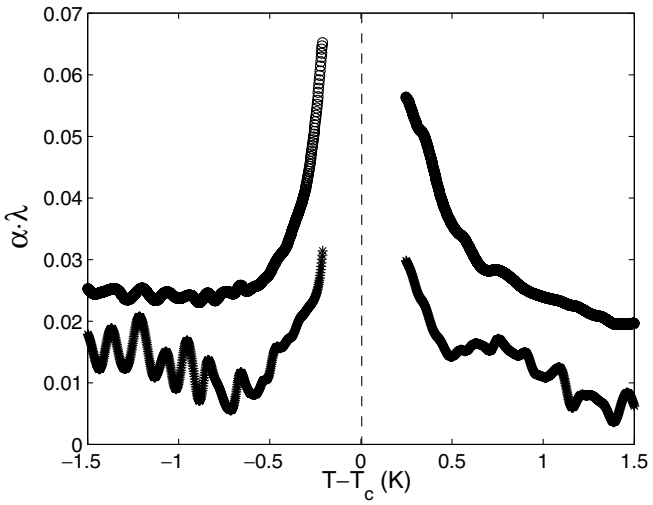

FIG. 3. Temperature dependence of the absorption coefficients per wavelength $\alpha_1\lambda$ and $\alpha_2\lambda$ at frequencies $f_1 = 107$ kHz (*) and $f_2 = 203$ kHz (○) in the vapor and supercritical phases for $\rho/\rho_c = 0.97$.

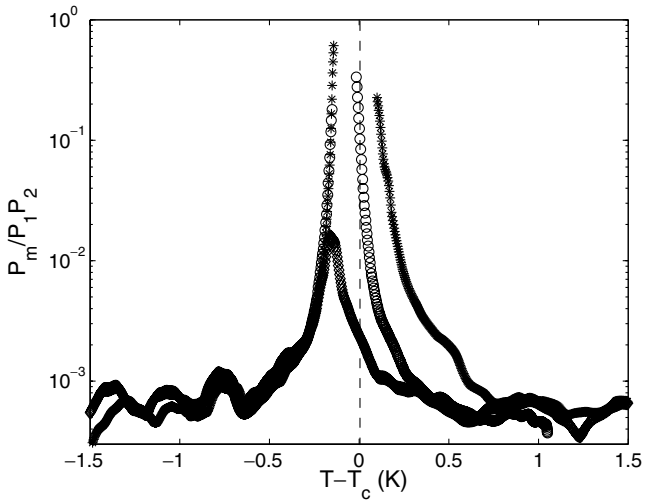

FIG. 4. Temperature dependence of the normalized amplitude P_m/P_1P_2 (arbitrary units) for three different densities: $\rho \approx 0.97\rho_c$ (*), $\rho \approx 0.95\rho_c$ (○), $\rho \approx 0.905\rho_c$ (◇).

$$A_m \propto \varepsilon \frac{(\omega_2 - \omega_1)L_{\text{int}}}{\rho c^3} A_1 A_2, \tag{1}$$

where ε is the acoustic nonlinearity parameter,

$$\varepsilon = \left(1 + \frac{B}{2A}\right), \tag{2}$$

where A and B are the coefficients of the linear and quadratic terms in the Taylor series expansion of the isentropic equation of state of the fluid [22,23],

$$A = \rho c^2, \qquad B = \rho^2\left(\frac{\partial c^2}{\partial \rho}\right). \tag{3}$$

For waves propagating in an absorbing medium, L_{int} should be replaced by a characteristic attenuation length $(\alpha_1 + \alpha_2)^{-1}$ [24]. There is also an additional geometrical factor when the wave vectors are not parallel [24,25]. We have displayed P_m/P_1P_2 as a function of temperature for the three densities $\rho/\rho_c = 0.905$, 0.95, and 0.97 in Fig. 4. We observe that this ratio strongly increases in the vicinity of T_c. As said above, the absorption is too large to allow measurements very close to T_c in the case of the two larger filling densities. The maximum of P_m/P_1P_2 is thus observed only with the lowest density $\rho \approx 0.905\rho_c$. Note also that P_m/P_1P_2 for different values of ρ first increase along the same curve below T_c, whereas the decrease at higher temperatures clearly depends on the density. Indeed, thermodynamic properties of the vapor phase do not depend on the filling density as long as the system is along the liquid-vapor coexistence curve. Note finally that the temperature domain around the CP where absorption cannot be measured is wider than the one where P_m/P_1P_2 cannot be measured because absorption measurements imply pressure measurements for $L = 160$ mm, i.e., with a signal attenuation larger than for $L = 107$ mm. It is the temperature domain of absorption measurements that ultimately fixes the temperature domain where the nonlinearity parameter can be determined.

Discussion and conclusion.—The experimental result displayed in Fig. 4 needs to be discussed before conclusions can be drawn about the behavior of the nonlinearity parameter in the vicinity of the CP where the medium becomes more and more absorbing. Indeed, the amplitudes P_1, P_2, and P_m that are measured are smaller than the ones in the scattering region where the two waves of amplitude A_1 and A_2 interact to generate the difference frequency wave of amplitude A_m. We may assume that the attenuations of the two waves at frequencies f_1 and $f_2 - f_1$ are similar and compensate since $f_1 \sim f_2 - f_1$, but the exponential attenuation of the wave at frequency f_2 on the propagation length $l \sim 30$ mm from the scattering region to the receiver clearly leads to overestimate A_m/A_1A_2 if the value of P_m/P_1P_2 is not corrected. We have to take into account the dependence of ρc^3 on T as well as the one of the attenuation length, $(\alpha_1 + \alpha_2)^{-1}$, which, as said above, replaces L_{int} in Eq. (1), since $(\alpha_1 + \alpha_2)^{-1} < L_{\text{int}}$ in our temperature range ($L_{\text{int}} = 30$ mm). We are thus left with

$$\varepsilon \propto \rho c^3(\alpha_1 + \alpha_2)\frac{P_m}{P_1P_2}\exp(-\alpha_2 l), \tag{4}$$

for the temperature dependent terms of ε. This is displayed in Fig. 5 which shows that the nonlinearity parameter increases roughly by a factor 10 at 0.2 K from the critical temperature. This is only in qualitative agreement with the theoretical prediction of Borisov *et al.* [18]. Indeed, the best fit of the form $a|T - T_c|^b + c$ gives $b = -2.3$ in the vapor phase and $b = -2$ in the supercritical phase whereas the predicted exponent is -0.89. This discrepancy could be ascribed to a possible overestimation of the absorption far from the CP due to the finite size

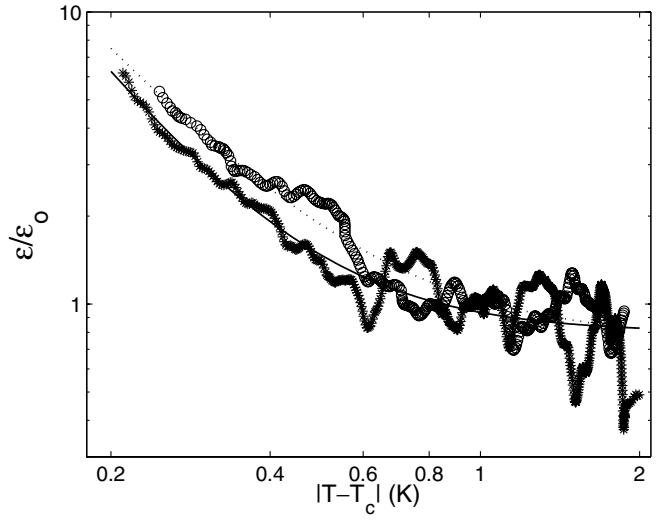

FIG. 5. Temperature dependence of the nonlinearity parameter ε normalized by its value ε_0 1 K away from the critical temperature: in the vapor ($*$) and supercritical ($\bigcirc$) phases. $\rho \approx 0.97\rho_c$. Best fits of the form $a|T - T_c|^b + c$ in the vapor phase (solid line, $b = -2.3$) and in the supercritical phase (dotted line, $b = -2$).

of the emitters, or to the complex behavior of the background contributions to the nonlinear parameter (e.g., sign changes). This requires further theoretical as well as experimental investigations.

Although the increase of the nonlinearity parameter in the vicinity of the CP is reported here for the first time, we note that the effect of a phase transition on acoustic waves has been also studied in other systems: reduction of velocity and enhancement of absorption and acoustic nonlinearities have been observed in the vicinity of phase transitions in ferroelectric and magnetic materials [26]. Nonlinear effects dominate the behavior of second sound sufficiently near the λ transition [27]. Surface waves at the liquid-vapor interface are also strongly modified in the vicinity of the CP [28]. It would be of great interest to find whether there exist generic features concerning the effect of phase transitions on the nonlinear properties of waves.

We thank Y. Garrabos for useful discussions and J. Da Silva Quintas for technical support. R.W. thanks the Centre National d'Etudes Spatiales for financial support. This work has been supported by Contract No. 02/CNES/0211/00-DPI190.

[1] See, for instance, *Supercritical Fluids Fundamentals for Applications*, edited by E. Kiran and J. M. H. Levelt Sengers, NATO ASI, Ser. E, Vol. 273 (Kluwer Academic, Dordrecht, 1994), and references therein.

[2] R. Folk and G. Moser, Phys. Rev. E **57**, 683 (1998); **57**, 705 (1998); G. Flossmann, R. Folk, and G. Moser, Phys. Rev. E **60**, 779 (1999), and references therein.

[3] A. Onuki, *Phase Transition Dynamics* (Cambridge University Press, Cambridge, 2002).

[4] See, for instance, the reviews in Chem. Rev. **99**, No. 2 (1999).

[5] C. M. Herget, J. Chem. Phys. **8**, 537 (1940).

[6] N. S. Anderson and L. P. Delsasso, J. Acoust. Soc. Am. **23**, 423 (1951).

[7] J. L. Kline and E. F. Carome, J. Chem. Phys. **58**, 4962 (1973).

[8] C. W. Garland and R. D. Williams, Phys. Rev. A **10**, 1328 (1974).

[9] C. W. Garland, D. Eden, and L. Mistura, Phys. Rev. Lett. **25**, 1161 (1970).

[10] H. Z. Cummins and H. L. Swinney, Phys. Rev. Lett. **25**, 1165 (1970).

[11] D. B. Roe, B. A. Wallace, and H. Meyer, J. Low Temp. Phys. **16**, 51 (1974).

[12] A. B. Kogan and H. Meyer, J. Low Temp. Phys. **110**, 899 (1998).

[13] M. Fixman, J. Chem. Phys. **33**, 1363 (1960).

[14] L. Kadanoff and J. Swift, Phys. Rev. **166**, 89 (1968).

[15] K. Kawasaki, Phys. Rev. A **1**, 1750 (1970).

[16] A. Onuki, Phys. Rev. E **55**, 403 (1997).

[17] J. K. Bhattacharjee and R. A. Ferrell, Physica (Amsterdam) **250A**, 58 (1998).

[18] Al. A. Borisov, A. A. Borisov, S. S. Kutateladze, and V. E. Nakoryakov, JETP Lett. **31**, 585 (1980); J. Fluid Mech. **126**, 59 (1983).

[19] P. C. Albright, T. J. Edwards, Z. Y. Chen, and J. V. Sengers, J. Chem. Phys. **87**, 1717 (1987).

[20] M. Barmatz and P. C. Hohenberg, Phys. Rev. Lett. **24**, 1225 (1970).

[21] E. W. Lemmon, M. O. McLinden, and D. G. Friend, "Thermophysical Properties of Fluid Systems," in NIST Chemistry WebBook, edited by P. J. Linstrom and W. G. Mallard, NIST Standard Reference Database No. 69, 2001, National Institute of Standards and Technology, Gaithersburg, MD 20899.

[22] R. T. Beyer, in *Nonlinear Acoustics*, edited by M. F. Hamilton and D. T. Blackstock (Academic Press, New York, 1998).

[23] L. Naugolnykh and L. Ostrovsky, *Nonlinear Wave Processes in Acoustics* (Cambridge University Press, Cambridge, 1998).

[24] P. Alais and P.-Y. Hennion, C.R. Acad. Sci. (Paris) **282**, B385 (1976); **282**, B421 (1976).

[25] V. A. Zverev and A. I. Kalachev, Sov. Phys. Acoust. **15**, 322 (1970).

[26] Yu. M. Sandler and O. Yu. Serdobol'skaja, Ferroelectrics **48**, 49 (1983); Yu. A. Kossevich, O. Yu. Serdobol'skaja, and E. S. Syrkin, Ferroelectrics **75**, 409 (1987); L. K. Zarembo, S. N. Karpachev, T. A. Ludzskaya, and I. V. Saenko, Phys. Solid State **39**, 570 (1997); O. Yu. Serdobol'skaja, A. V. Serdobol'skii, and G. P. Morozova, Phys. Solid State **42**, 528 (2000).

[27] L. S. Goldner, N. Mulders, and G. Ahlers, J. Low Temp. Phys. **93**, 131 (1993); L. C. Krysac, Phys. Rev. Lett. **73**, 2480 (1994).

[28] S. Fauve, K. Kumar, C. Laroche, D. Beysens, and Y. Garrabos, Phys. Rev. Lett. **68**, 3160 (1992); R. Wunenburger, P. Evesque, C. Chabot, Y. Garrabos, S. Fauve, and D. Beysens, Phys. Rev. E **59**, 5440 (1999).