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Nonsingular absorption of ultrasound near the critical mixing point of a binary liquid

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The absorption and velocity of ultrasound and the critical opalescence have been measured for a critical-composition mixture of nitrobenzene and 2,2,4-trimethylpentane along the critical isochore in the homogeneous phase of the system. The measurements cover the relatively wide range of temperature interval of 30 K to 7 mK from the critical value. The nearness of approach to the critical point was affirmed by the critical-opalescence measurements. The measurements of acoustic absorption covered the range of 1 to 91 MHz, and the strong frequency dependence observed can be satisfactorily described by the Fixman-Kawasaki theory with the adjustment of three parameters. Singular behavior for the sound absorption, consistent with critical slowing down, was observed when the mixture was more than about 3 K away from the critical point. When within about 0.3 K of the critical temperature the sound absorption was observed to become constant. The absence of any effects on the critical sound absorption, while the mixture was under a large electric field, is also reported.

I. INTRODUCTION

It has long been known that high-frequency sound is strongly absorbed near the critical points of numerous one-component fluid systems and near the critical mixing points of various binary liquid mixtures. Despite considerable progress in recent years, the detailed mechanism of this critical absorption is still not well understood theoretically,[1-3] nor particularly well characterized experimentally.[4-8] This critical absorption is observed to become increasingly dependent on the frequency of the sound as the critical point is approached along the critical isochore in the homogeneous region. Measurements of absorption over several decades in sound frequency are required before reasonable tests of absorption theories are possible. Absorption near a critical point can be quite large, and frequency-dependent noncritical contributions are often present, thus compounding the difficulty of such measurements.[6]

Suggested originally by Fixman[8] and later improved by Kawasaki[9] and then Mistura,[10] the most widely successful theory of critical sound absorption assumes that a coupling of the sound transport mode and the mass-diffusion mode is established by the critical concentration fluctuations in binary liquid mixtures. The fluctuation spectrum near a critical point is characterized by the rate of decay of the fluctuations, which, in binary mixtures, is the mass diffusion over a distance of the correlation length for the fluctuations. Hence this diffusion rate, or frequency, determines the characteristic frequency of the critical sound-absorption spectra. The mode-mode coupling theory of dynamic critical phenomena[11] suggests that the mass-diffusion mode of a binary mixture approaching the critical point should slow down, and static scaling theory[12] indicates that the correlation length should increase. Both of these should occur in such a way that the characteristic frequency of the critical sound-absorption spectra should decrease as the critical point is approached, with a scaling exponent of about 1.89 in the Ising lattice-gas model. In general, true critical behavior may only be expected to occur very close to the critical point where noncritical phenomena have been scaled to insignificance. Some sound-absorption spectra reported previously for binary liquids[4,6,7,10] show approximately the predicted scaling effect on the characteristic frequency for reduced temperatures $\epsilon = (T - T_c)/T_c$ ranging from about 10^{-1} to 10^{-3}, with some expected exceptions.[13] Properly tested, this scaling should also be measured much closer to the critical point in systems that can be demonstrated unambiguously to indeed be approaching the critical point.

Recently an apparent contradiction between the theory of critical sound absorption and experimental observations was reported by Harada *et al.*[1] They pointed out that starting with an assumption of scaling for the characteristic frequency and amplitude of absorption, and then calculating sound absorptions at various frequencies using the Fixman-Kawasaki theory, with mode-mode coupling assumptions, gives an absorption that initially increases as the critical point is approached, but then peaks and falls dramatically to zero at the critical point. This peak and rapid decline is much more pronounced at lower frequencies (1 or 2 MHz) and might occur as much as several tenths of a degree Kelvin prior to the critical point. As they pointed out nothing of this sort has previously been reported in real systems.

The spatial symmetry of a critical system is expected to be one of the few things that determines which universality class the particular system belongs to.[12] It is ordinarily assumed that one-component fluid and binary-mixture systems would all belong to the Ising lattice-gas universality class, being symmetrical in the three spatial dimensions and having only short-range interparticle forces. Many of the binary mixtures known to have a nonmiscibility gap are mixtures of a polar-molecule liquid with a nonpolar liquid. Polar molecules are nonsymmetrical and have long-range interaction forces. It has been suggested that the rapid tumbling of the polar molecules in the liquid may be responsible for the fact that static scaling exponents for polar + nonpolar liquid mixtures seem to have Ising lattice-gas values.[14] Debye and Kleboth[15] have reported that the application of a large electric field to critical mixtures of nitrobenzene and 2, 2, 4-trimethylpentane, when sufficiently near the critical temperature, caused the effective critical temperature, as measured by critical opalescence, to shift to lower values. They applied pulsed electric fields of up to 45 kV/cm, when the sample was within 0.1 K of the critical temperature, and found a decrease in the opalescence which amounted to several percent. For noncritical mixtures the thermal free energy of concentration fluctuations away from the equilibrium value is much larger than would be the electric field energy for the polar molecules, using currently attainable fields in the laboratory.[15] However, very near the critical point the energy barrier to fluctuations decreases dramatically and a more reasonable electric field may have an effect. Similarly, if the mass diffusion depends on the symmetry of the molecular system, then near the critical point one might hope to observe an effect upon the critical sound absorption caused by an electric field.

Previously, Anantaraman *et al.*[16] reported measurements of sound absorption in nitrobenzene + 2, 2, 4-trimethylpentane near the critical point. Although they saw strong frequency-dependent absorption as the critical point was approached, the limited frequency range of their measurements (4.6 to 16.5 MHz) severely limited the comparisons that could be made with critical absorption theories. The temperature range of their measurements came no closer to the critical temperature than 0.3 K ($\epsilon = 10^{-3}$) and no further away than 15 K ($\epsilon = 5\times 10^{-2}$), while their temperature regulation near the critical point was ± 50 mK.

The present measurements have attempted a more definitive measurement of the characteristics of the critical absorption of sound in the critical mixture nitrobenzene and 2, 2, 4-trimethylpentane. These measurements span two decades in sound frequency (1 to 91 MHz) and almost four decades in reduced temperature. The critical opalescence of this system was also monitored, in order that a close approach to the critical point might be verified independent of the sound measurements. It was felt that this was imperative, considering the difficulties of properly preparing a mixture with the critical concentration, the difficulties of temperature regulation in the range of ± 1 mK, and the possible dependence of the critical temperature upon trace impurities in the sample which gives each sample prepared its own unique, and unknown, critical temperature.[17] In addition, the sound absorption in this mixture was tested for changes, upon the application of a large electric field, that might indicate symmetry-dependent effects near the critical point, where again a very close approach to the critical point was essential.

First in this paper will be a brief review of the Fixman-Kawasaki theory of critical sound-absorption spectra. Next the apparatus and techniques used in the present measurements will be described, followed by representative examples of the data gathered in this study. The temperature dependence of the parameters characterizing the complete set of data will then be discussed in relation to previous results, and as to their impact on our understanding of critical absorption and critical phenomena.

II. CRITICAL ABSORPTION THEORIES

Frequency-dependent sound propagation near critical points was conveniently expressed in terms of a relaxing complex heat capacity by Fixman[8] and later by Mistura,[10] or in terms of a relaxing complex viscosity by Kawasaki.[9] Critical fluctuations couple the relaxing heat capacity or viscosity to the mass-diffusion mode in binary mixtures, hence the total effect on the sound is that due to a Gaussian distribution of independent fluctuations. Summing over all fluctuations gives the following complex integral for the multiply relaxing complex heat capacity or viscosity:

$$\eta(f^*) = \int_0^\infty \frac{x^2}{(1+x^2)^2}\frac{1}{K(x) - if^*}\, dx\,, \tag{1}$$

where the integration is taken over the variable $x = k\xi$, for k the fluctuation wave number and ξ the fluctuation correlation length. The frequency dependence of Eq. (1) is in $f^* = f/f_D$ where f is the sound frequency, $f_D = D/\pi\xi^2$, and D is the mass-diffusion coefficient. The function $K(x)$ was taken by Fixman to be $x^2(1+x^2)$ and later by Kawasaki to be $3/4[1 + x^2 + (x^3 + x^{-1})\arctan(x)]$. These two forms differ only for large values of x, which make a significant contribution to the integral only when f^* is large.

The real part of $\eta(f^*)$ in Eq. (1) gives the critical sound absorption, and the imaginary part the sound dispersion. Hence,

$$(\alpha/f^2)_{\mathrm{CP}} = [2\pi A(T)/u_0 f_D]\ \mathrm{Re}\,\eta(f^*) \tag{2}$$

is the critical-point absorption α per square frequency, where $A(T)$ is a dimensionless amplitude depending only on thermodynamic quantities according to

$$A(T) = \frac{k_B T^3}{2\pi\rho^3}\frac{1}{u_0 C_v^2}\left(\frac{\partial P}{\partial T}\right)_v^2 \xi^{-1}\left(\frac{\partial \xi^{-1}}{\partial T}\right)^2 \tag{3}$$

for k_B Boltzmann's constant, ρ the density, u_0 the low-frequency sound velocity, C_v the constant-volume specific heat, P the pressure, and T the absolute temperature.[10]

In the work of Fixman and Kawasaki, the Ornstein-Zernike form of the correlation function for the critical fluctuations was used in formulating $\eta(f^*)$. It is not expected that this form should be valid for $f^* \gg 1$, and indeed, in measurements[5] on one-component fluids near their critical point, data for large f^* do not agree with Eq. (2). Such a discrepancy has not yet been clearly observed in binary mixtures, and presumably is not seen since critical dispersion effects in binary mixtures are quite small.[4,6-8]

In laboratory measurements on real fluids Eq. (2) is often not sufficient, since other noncritical processes may also contribute to the measured sound absorption. Two common contributions are the classical Navier-Stokes absorption, due to the viscosity and thermal conductivity of the fluid, $(\alpha/f^2)_{\mathrm{NS}}$; and single-relaxation absorption due to chemical or thermal processes in the fluid, $(\alpha/f^2)_{\mathrm{SR}}$. Assuming the possibility of more than one single-relaxation process in the system, the total observed absorption may have the form

$$(\alpha/f^2)_{\mathrm{tot}} = (\alpha/f^2)_{\mathrm{CP}} + \sum (\alpha/f^2)_{\mathrm{SR}} + (\alpha/f^2)_{\mathrm{NS}}\ . \tag{4}$$

The Navier-Stokes term is frequency independent, so if all single-relaxation processes in the fluid are sufficiently weak in amplitude, or at frequencies well above or below the region of inquiry, then the critical term may be the only one giving a measurable frequency dependence. In such a case we can put all the quantities independent of f into a single term $B(T)$ and write

$$(\alpha/f^2)_{\mathrm{tot}} = (\alpha/f^2)_{\mathrm{CP}} + B(T)\ , \tag{5}$$

whereupon it is very convenient to collect all the temperature dependent terms in Eq. (5), using Eq. (2), and write them as a temperature-independent reduced absorption per wavelength,

$$\begin{aligned}(\alpha\lambda)^* &= [(\alpha/f^2)_{\mathrm{tot}} - B(T)]u_0 f A(T)\\ &= 2\pi f^*\ \mathrm{Re}\,\eta(f^*)\ .\end{aligned} \tag{6}$$

It is a common, although not ideal practice,[6] that was followed in the present work, to treat $A(T)$ as a fit parameter when data for $(\alpha/f^2)_{\mathrm{tot}}$ at various frequencies were evaluated with the Fixman-Kawasaki theory of Eqs. (2) and (5). This was necessitated in the present study, by the lack of data on the thermodynamic quantities contained in Eq. (3). The absorption data reported here have been analyzed with Eqs. (2) and (5), allowing $A(T)$, $B(T)$, and f_D to be chosen so as to give the lowest standard deviation for fits to the data. The Kawasaki from of $K(x)$ was used in these fits. Numerical integration and parameter search algorithms were written and implemented on a DEC PDP/10 system.[18]

III. EXPERIMENTAL TECHNIQUE

Spectroscopic-grade nitrobenzene and 2,2,4-trimethylpentane were purged of dissolved oxygen by bubbling with dry nitrogen gas, but were not otherwise cleaned in preparation of the sample. The composition of the sample was determined by weighing the pure liquids while contained in the syringe used to inject the liquids into the cell. Thus determined, the final composition of the sample used was 0.51606 ± 0.0001 weight-fraction nitrobenzene. Others who have worked with these mixtures have reported a critical composition of 0.515 ($T_c = 303.4$ K) (Ref. 16) and 0.517 ($T_c = 302.3$ K).[15] The sample cell was evacuated to less than 1 μ Hg, and backfilled with dry helium gas prior to injecting the sample. While in the cell the sample came only in contact with inert materials.

The sample cell was made of a Pyrex-glass tube (see G in Fig. 1) with a quartz-glass rod (Q) sealed to the tube bottom with a fluorocarbon O ring (R). A stainless-steel top plate (P) fitted with

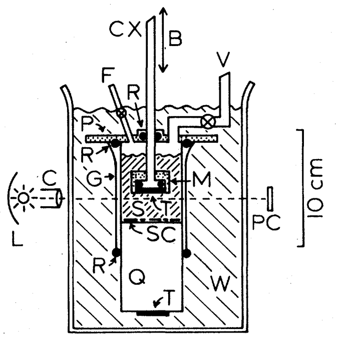

FIG. 1. Schematic diagram of the sample cell: S, liquid sample; T, transducers; Q, quartz rod; G, glass cell walls; M, mount for transducer; P, cell top plate; R, O-ring seals; CX, coaxial transmission line; B, translator bed; V, vacuum system connection; F, sample fill line; SC, wire mesh screen; W, water bath; L, lamp; C, collimator; PC, photoresistive cell.

a vacuum pump line (V), and sample-injection fill line (F), had an O-ring slip joint to allow the stainless-steel tube upper-transducer support to be slid vertically through the plate. The tubular transducer support doubled as a coaxial transmission line (CX) from the upper transducer (T), which was in contact with the liquid sample, to the bed of the micrometer translater (B). The generated ultrasonic wave, after leaving the upper transducer, passed downward through the sample liquid and into the quartz rod, whereupon it was delayed by about 12.5 μsec before reaching the lower transducer outside the cell. The transducers used were 1-MHz fundamental, overtone polished, matched, gold plated, quartz crystals. The arrangement of the sample cell ensured that both crystals were at the same temperature at all times during each set of measurements, so that the crystal operating frequencies would remain matched.

The entire cell, including all regions that were accessible to the sample vapor, was immersed in a constant-temperature stirred water bath (W). The walls of the water-bath container were made of glass, covered with insulation through which openings were made to observe the sample periodically during the measurements. A white-light beam, approximately 1 cm in diameter, generated by the lamp (L) and collimator (C), passed horizontally through the bath and sample. The transmitted-light intensity could be monitored by a photoresistive cell (PC).

A nickel-chromium wire-mesh screen (SC) inside the sample cell rested on the top of the quartz rod. The wire-repetition distance for the square mesh grid was 1.6 mm, which was larger than the longest wavelength for the sound in these studies. It was determined in a separate measurement that the wire mesh itself had no observable effect on the sound-absorption spectra from 1 to 91 MHz. A very small diameter wire was connected to the wire mesh, passed to the outside of the cell through the lower O ring, and then connected to a high-voltage transmission line. The wire-mesh screen thus allowed high electric fields to be established in the sample between the screen and the electrically grounded upper transducer.

Bursts of rf, a few microseconds in duration, were generated with a Matec 6600 ultrasonic pulse modulator[19] and delivered to the upper transducer as shown in Fig. 2. The received signals from the lower transducer were then amplified and detected by the Matec system. The pulse-train envelope, occurring after each generator pulse and having arrived at the receiver output, was summed with a dc comparison voltage before being displayed by an oscilloscope. The comparison voltage, which was measured by a digital voltmeter, allowed accurate peak-height measurements of the received pulses. A silicon-controlled-rectifier (SCR) pulser and pulse transformer, triggered along with the sound bursts (see Fig. 2) was the source of the large electric fields established in the sample between the wire mesh and the upper transducer. The high voltage pulses placed on the sample were adjustable from 0 to about 20 kV, and were approximately sine-wave shaped with a half-height width of about 30 μsec. The repeating trigger pulse from the master trigger source went directly to the SCR pulser, and via a time delay, to the rf pulse generator. This allowed delaying the rf burst so that the sound would be passing through the sample during the few microseconds near the peak-height time for the electric field, the coincidence of which could be observed on the oscilloscope.

Sound-absorption measurements were made by the variable path-length method with typically 7 to 10 settings of the translator bed, and corresponding readings of the pulse height. Only the first pulse of sound, observed to pass through the sample after each burst of rf, was used in these measurements, thus avoiding any pulse overlap interference (except for extremely short liquid path lengths which were avoided). A least-squares fit, performed immediately on each set of path lengths and pulse amplitudes, yielded an absorption coefficient. The precision of each such measurement of absorption was greater than ±2%, and its repeatability was better than ±5%, except at 1 MHz.

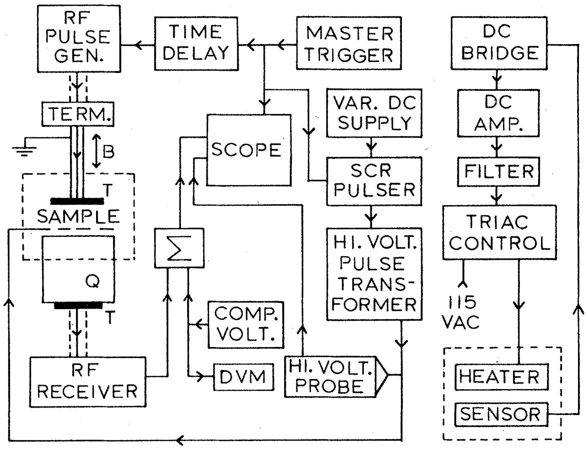

FIG. 2. Ultrasonics and temperature-control circuitry. The sample cell appears on the left side of the figure with transducers, T; quartz rod, Q; and translator bed, B. Arrows indicate the direction of flow of pulses or processed information. The temperature-control system appears on the right side of the figure, where a dashed line indicates the water bath.

At the fundamental frequency of the transducers, observable diffraction of the sound wave occurred. Correction for this effect was made in the usual way.[4,13,20] The accuracy of this ultrasound spectrometer was found to be about ±5%, except for small values of absorption at 1 MHz, by test measurements performed on various samples known to have frequency-independent absorptions between 1 and 100 MHz. The single pair of crystal transducers discussed above was found to provide satisfactory absorption measurements from 1 to 91 MHz, provided that the range of path lengths chosen for each frequency was adjusted properly.

Measurement of the effect of a large electric field on sound absorption in the liquid sample was only tested at a few sound frequencies. For these measurements the repetition rate of the master trigger was reduced to about 5 Hz, and the high voltage turned on for only a few pulses. This was necessary, since the conductivity of this sample was low enough that additional application of the high voltage would have caused sample heating that could have been significant near the critical point of the sample.[15] Typically, the upper transducer was placed a few millimeters above the wire mesh screen, and then held stationary, while sound pulse heights were monitored with and without the high voltage applied.

The velocity of sound in the sample was measured by varying the liquid path length, while measuring the time delay for the arrival of the first pulse of sound to traverse the liquid. This travel time in the liquid was found by monitoring the time location of the pulse peak on the oscilloscope, again using the comparison voltage to enhance the sensitivity, with the oscilloscope's adjustable internal time delay measured by a digital time-interval clock. Such measurements were only accurate within ± 0.1%.

Absolute measurements of the water-bath temperature in the vicinity of the sample cell were made with a platinuum resistance thermometer, calibrated to within ± 0.01 K. The thermometer's resistance was monitored continuously using a very low-drift (± 50 ppm) constant-current source and digital voltmeter, capable of measuring the thermometer's temperature within ± 0.04 K.

The temperature of the water bath was regulated with a separate resistance thermometer and proportionally controlled electric heater. The general circuit configuration of the temperature regulator is shown in Fig. 2. The sensor was an encapsulated thermistor, with a large thermal coefficient, acting as one arm in a dc Wheatstone bridge. The bridge balance condition was monitored with a dc amplifier, having a nominal voltage gain of 10^5, and an input amplifier of differential configuration with a very high input impedance and very low drift (± 0.4 μV per month). The amplifier output passed through a notch filter, set approximately to the natural thermal resonance frequency of the regulator-bath system (about 50 sec period), and into a triac ac phase control to proportionally provide ac power to a 500-W immersion heater. The bath, of about 26l capacity, was rapidly stirred with the thermistor located near the stirring device to minimize response time for both heating and cooling. Temperature control within ± 3 mK was realized for temperatures more than 10 K above room temperature, which includes the 333 and 318 K data reported for the present sample. However, regulation within ± 1 mK was possible for temperatures nearer room temperature, which included data from about 306 K down to the critical temperature for the present sample.

For the present measurements, the sample was allowed at least 2 hours equilibrium time, after changing the bath temperature, and near the critical point about 10 hours was common. Soon after each temperature change, the upper transducer was uncoupled from the translator bed and moved up and down relatively rapidly so as to stir the sample and ensure more uniform mixing. Visual observations of the sample, and measurements of the transmitted-light intensity by the photoresistive cell, provided further evidence of sample homogeneity and equilibration. Light-transmission intensity measurements were not of high precision, but could easily be made stable and repeatable within ± 10% relative to the transmitted intensity far from the critical point of the sample.

IV. RESULTS AND DISCUSSION

Reported here are measurements of the sound absorption and velocity, as well as the critical opalescence, or light absorption, for a single mixture of nitrobenzene and 2, 2, 4-trimethylpentane with the concentration of 0.516 weight-percent nitrobenzene. The measurements were made at eleven temperatures all above the critical temperature, where the mixture was in its homogeneous single phase. The sample was prepared at room temperature in the manner described in Sec. III, whereupon it was warmed to its highest temperature (333 K), mixed, allowed to equilibrate and cooled in steps toward the critical temperature. After first observing phase separation, the mixture was reheated to its highest temperature, the data checked for repeatability, and the temperature again lowered in steps toward the critical value. This was done a total of three times, with the nearness of approach to the critical temperature improved each time. The phase separation temperature observed for these three temperature cycles increased a total of approximately 0.2 K over the course of the three cycles. This was presumably due to either or both an increasing sample-impurity effect or a platinum-thermometer measurement drift. The measured critical opalescence was observed at all times to be a very sensitive indicator of the nearness of the critical point, especially when the temperature was within a few tenths of a degree Kelvin of T_c. No long-term drifts were observed in the opalescence, after the initial transients following a purposeful change in the bath's temperature. Thus, it is concluded that the different phase-separation temperatures, observed for the three temperature cycles, could not have been caused by increasing impurities in the sample while near the critical temperature; and that those data for small ϵ values do indeed represent equilibrium measurements within the limits of temperature regulation.

The more commonly observed features of sound absorption and velocity near a critical mixing point are seen in Figs. 3 and 4. The absorption measured in the present critical mixture, is shown in Fig. 3 at various temperatures for two different sound frequencies. The anomalous absorption of sound clearly occurs much more strongly at lower frequencies as the critical point is approached. In Fig. 4 are reported the measurements for sound velocity in the critical mixture as the temperature approaches the critical value. Such a linear dependence of u_0 on T, with an absence of anomalies at T_c, is to be expected for binary mixtures.[4,8] The data shown were taken at 3 or 9 MHz: no dispersion ever being observed in this mixture, again an expected result for a binary mixture.

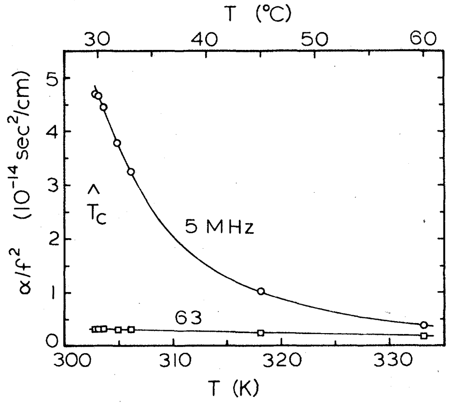

FIG. 3. General temperature dependence of the measured sound absorption in the 0.516-weight-percent mixture of nitrobenzene and 2,2,4-trimethylpentane as the critical temperature, T_c, is approached from higher temperatures. The absorption for 5-MHz sound is shown by the round symbols, and that for 63-MHz sound by the square symbols. The smooth lines drawn through the data points are visual aids only.

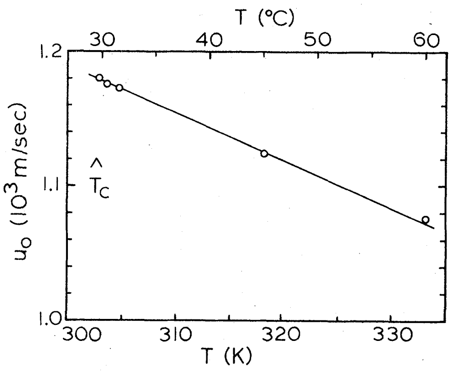

FIG. 4. The low-frequency sound velocity for temperatures approaching T_c in the critical-concentration mixture. These measurements were made at 3 or 9 MHz, there being no observable difference.

Least-squares fits of the Fixman-Kawasaki theory of Eqs. (2) and (5) were made using the full spectrum of data measured at each temperature, and three representative examples are

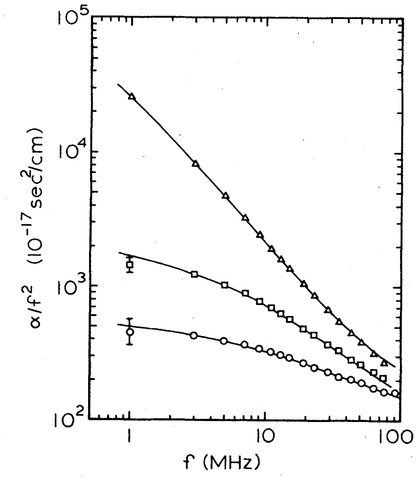

FIG. 5. Sound-absorption spectra for the critical mixture at three temperatures approaching T_c. The triangular symbols show measurements at $T \simeq 303.1$ K ($\Delta T \simeq 7$ mK, and $\epsilon \simeq 2.3 \times 10^{-5}$). The square symbols show measurements at $T \simeq 318$ K ($\Delta T \simeq 15$ K, and $\epsilon \simeq 5 \times 10^{-2}$). The round symbols show measurements at $T \simeq 333$ K ($\Delta T \simeq 30$ K, and $\epsilon \simeq 10^{-1}$). The lines passing through the three data sets are least-squares fits to the data using the Fixman-Kawasaki theory. The uncertainty for all the measurements is within the symbols shown, except the two data points for 1 MHz at the high temperatures where error bars are shown.

shown in Fig. 5. Uncertainties in the absorption measured for 1-MHz sound at 318 and 333 K, due to the relatively large size of the diffraction corrections, are indicated in the figure. For only these two temperatures the 1-MHz data were not used in making the fits. The highest curve in Fig. 5 was fit to data taken at about 303.1 K ($\Delta T \simeq 7$ mK), the closest approach to the critical point reported in the present study. As is apparent qualitatively in Fig. 5, the theory of Eqs. (2) and (5) can be made to fit well to the present data over the full range of temperatures investigated. To test this conclusion, single-relaxation theory fits were attempted on the same data, but the quality of the fits was very clearly inferior.

Sound-absorption measurements were also made with the same apparatus on pure liquid nitrobenzene and then on pure 2, 2, 4-trimethylpentane both at 303 K. The spectra from 3 to 91 MHz showed no frequency dependence within the precision of the apparatus. In both cases the measured absorption was $(75.5 \pm 1) \times 10^{-17}$ sec^2/cm. All the measurements on the critical mixture, within their precision, showed no evidence of any frequency dependence other than that attributable to the critical effects. This, coupled with the strength and range of the critical effects on sound absorption, made this mixture well suited for this type of measurement.

To test further the effectiveness of Eqs. (2) and (5) to describe satisfactorily the frequency dependence of the measured absorption in this critical mixture, the data were analyzed according to the scheme of Eq. (6). The results of this are shown in Fig. 6 as reduced absorption per wavelength at various reduced frequencies. Somewhat less than half of the sound-absorption data that make up the present study are shown in the figure, and those data were chosen to be representative over the full range of temperatures investigated. In Fig. 6 it is also seen that Eqs. (2) and (5) remain a satisfactory fit to the present measurements for f^* well above 10^2, as has been previously reported for other binary mixtures, but not for one-component fluids.[4,5,8] The data in Fig. 6 have one of the largest ranges of f^* yet reported for any binary mixture and to this extent are a strict and successful test of the applicability of Eqs. (2) and (5). Again it is noted that the inability to calculate $A(T)$ from the parameters of Eq. (3) makes the present study a less than complete test of the Fixman-Kawasaki theory.

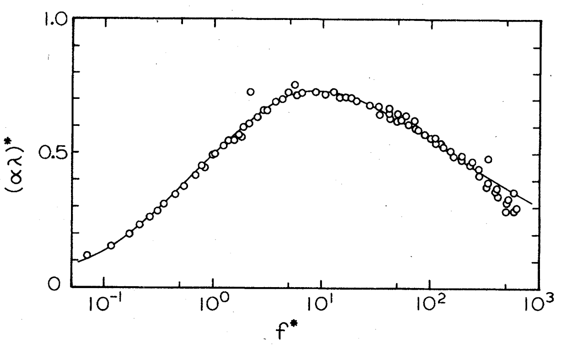

FIG. 6. Measured reduced absorption per wavelength in the critical mixture for various reduced frequencies. The data shown are representative points chosen from data taken at all the temperatures reported here ($T_c \lesssim T \lesssim 333$ K). The line drawn through the data is a least-squares fit to the Fixman-Kawasaki theory using Eq. (6).

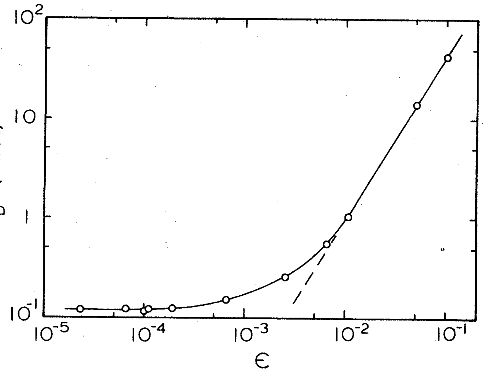

FIG. 7. Reduced-temperature dependence of the parameter, f_D, obtained from fits to the present data for the critical mixture. The straight solid line with its dashed-line extrapolation is a scaling behavior fit to the three data points of highest ϵ. The curved solid line passing through the remainder of the data is a visual aid only.

For each of the eleven distinct temperatures at which a sound-absorption spectrum was recorded, fits of Eqs. (2) and (5) yielded optimum values for the parameters, i.e., values of $A(T)$, $B(T)$, and f_D. In Fig. 7 are shown the results for the parameter f_D, the characteristic frequency. The statistical quality of the fit to each set of data was such that the estimated standard deviation for the reported values of f_D was ±10%. This

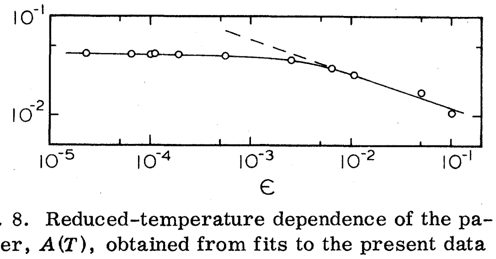

FIG. 8. Reduced-temperature dependence of the parameter, $A(T)$, obtained from fits to the present data for the critical mixture. The various lines passing through the data points have the same significance as those in Fig. 7.

figure will be discussed in more detail presently.

The results of fits to data on the present critical mixture provided the values for $A(T)$, the critical amplitude, shown in Fig. 8. The estimated standard deviation for the $A(T)$ parameter is ±1%, which is much better than for f_D, due to the nature of Eqs. (**2**) and (5), and the fact that the data were gathered over no more than 2 decades in frequency. The values of the parameter $B(T)$, indicated most appropriate by the fits to the data, were about 1 or 2 times the absorptions measured for the components of the mixture in their pure forms. This is further evidence that the only measurable frequency dependence in this critical mixture, over the ranges investigated, was that due to the critical effects.

During the time that the critical mixture was at each of the temperatures for which sound-absorption measurements have been reported here, the relative intensity of white light, transmitted through the sample, was also measured. The exponential light-absorption coefficient α_l was measured, relative to the intensity of light transmitted through the mixture at its highest temperature in this study (333 K). No measurable change in intensity occurred between 333 and 318 K, but as the temperature was lowered to each new value below 318 K, the opalescence noticeably increased; often to the extent that the change was apparent to the unaided eye. In Fig. 9 are shown the results of these relative intensity measurements at various temperatures approaching the critical value. The quantity α_l has arbitrary units, since it is only a relative measure. For the three measurements of light absorption at the highest temperatures in Fig. 9, the measurement uncertainty is considerably larger than for the remainder of the measurements, since in this region the sample was only slightly more opalescent than it was at the transmission reference temperature of 333 K (not shown in the figure).

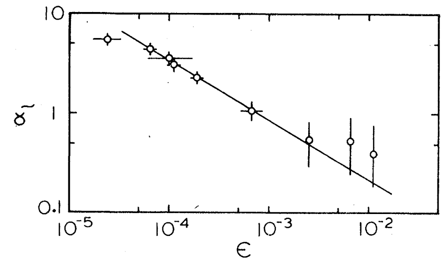

FIG. 9. Reduced-temperature dependence of the absorption coefficient for white light measured in the same critical mixture concurrently with the sound-absorption measurements. Error bars for the light absorption and temperature measurements are shown for each data point. The straight line passing through the points is a fit to the data assuming a scaling behavior.

While not of high precision, the light-absorption measurements performed concurrently with the sound-absorption measurements, demonstrated unambiguously a very important point about the mixture, and the measurements made on it that are reported here. That is, this sample mixture was indeed progressing toward the critical point as the temperature was lowered over the full range of the investigation, with the possible exception of the lowest-temperature α_l measurement, where the early signs of rounding may be showing. As mentioned in Sec. I, it requires great experimental care to approach a critical point very closely, and only a critical divergence of some relatively directly measurable physical parameter can be taken as reasonable proof of a close approach. Indeed, the critical point is its own absolute reference point in thermodynamic space.

A comparison of Figs. 7 through 9 reveals some surprising observations for the sound-absorption measurements on this mixture. The reduced-temperature axes in Figs. 7 through 9 are identical, except for truncation one decade sooner on the high temperature end for the light data in Fig. 9. The data in Figs 7 and 8 show the qualitatively expected behavior of scaling over the region of approximately $10^{-2} < \epsilon < 10^{-1}$. In Fig. 7 the slope of the straight-line fit through the three highest-temperature data points is 1.6 ± 0.1. This is not too different from the value 1.89 predicted by mode-mode coupling and Ising lattice-gas theories,[4,7,13] especially considering that the experimental value was determined with only one decade of change in ϵ. Likewise, in Fig. 8 the three highest-temperature points seem to have a scaling behavior, and they yield an exponent of -0.5 ± 0.1. As has been noted before,[4,7,13] the usual scaling theory expectation is that $A(T)$ scales with an exponent greater than or equal to about -0.110. Again, the present experimental value, over the limited high-temperature range in ϵ, appears in reasonable agreement under the circumstances. For $\epsilon < 10^{-2}$ the results seen in Figs. 7 and 8 appear to show the mixture no longer approaching the critical point (or an incorrect choice of T_c), while for Fig. 9 the mixture is certainly still progressing toward the critical point as ϵ is lowered. It is noted here that the independence of f_D and $A(T)$ from ϵ, below $\epsilon \simeq 5 \times 10^{-4}$, is not an artifact of the fitting of Eqs. (2) and (5) to the measured sound-absorption data. This must be true, since for each single frequency of sound measured, at the temperatures in this region, no measurable change in absorption occurred. It is clear, then, that sound absorption in this mixture is showing nonsingular behavior in the region of approximately $2\times 10^{-5} < \epsilon < 10^{-3}$.

One might speculate initially that the nonsingularity in f_D could be explained by a nonsingularily in the diffusion coefficient D, and that further measurements in that area might prove fruitful. Certainly it would not be expected that ξ, which also appears in the expression for f_D, is nonsingular, since this quantity and its scaling have been well studied by light scattering in numerous systems. Indeed, the present measurements show a singularity in the critical opalescence. However, the nonsingularity in $A(T)$ is perhaps the most surprising since, according to Eq. (3), it is dependent entirely upon thermodynamic parameters and not on any of the transport coefficients, whose critical behavior is in general much less well understood at present.[11,17] Some of the qualitative features of the calculations by Harada *et al.*[1] are suggestive of the results of the present measurements. According to their calculations, the measured sound absorption at a few MHz should not only stop increasing as the critical point is approached, but should also begin a rapid decline when within approximately a few tenths of a degree Kelvin of T_c. As they mentioned, such an effect has not been observed experimentally, and in the light of the present measurements, this would seem to be a consequence of previous experiments not having approached the critical point closely enough. It seems apparent then, that there must be some fundamental difficulty with the application of the mode-mode coupling theory to critical acoustic phenomena in binary mixtures very close to the critical point.

While the critical mixture was at each of the temperatures reported here, and after the measurement of the sound-absorption spectrum, the sound velocity, and the white-light absorption, a check was made for the presence of any effect on the sound absorption by the large pulsed electric field. No such effects were ever observed. Following the calculations of Debye and Kleboth,[15] the effect was anticipated for measurements made within about 0.1 K of T_c and for electric fields of 45 kV/cm. If such an effect were present for the sound absorption, it would be expected to be most apparent at the lower frequencies where the critical effects are most pronounced. Most of the checks for an electric field dependence were made with 1 or 3 MHz sound. The most definitive test made for this effect on the present mixture was at 20 mK above the critical point with an applied electric potential of 12 kV and an electrode spacing (wire mesh and transducer ground plate) of 1 mm. Since the effect reported by Debye and Kleboth[15] was observed to diverge at the critical point, and depended on the square of the electric field, the corresponding effect on sound absorption, if any, must be much weaker. In consideration of the absence of a strong effect, it is observed that the induced asymmetry in the critical mixture must not couple strongly to the acoustic critical behavior. If, however, as was suggested earlier in this report, the critical sound absorption becomes nonsingular very near the critical point, then the absorption may no longer be sensitive to changes in the mass diffusion such as might occur under the influence of an electric field.

V. CONCLUSIONS

The critical mixture of nitrobenzene and 2, 2, 4-trimethylpentane has proved to be an ideal one for critical sound-absorption studies, since the only observed frequency dependence of the absorption could satisfactorily be ascribed entirely to the critical effects. The measured frequency dependence was well fit by the Fixman-Kawasaki theory with the adjustment of three parameters. The lack of thermodynamic data on the critical mixture precluded calculating the Fixman-Kawasaki parameters directly. Large pulsed electric fields established in the sample, while very near the critical point, failed to show any effect on the sound absorption. Thus, the mechanisms of critical sound absorption are not sensitive to the physical symmetry of the critical system very near the critical point.

Critical-opalescence measurements, performed concurrently with the sound-absorption measurements, demonstrated unambiguously that the present measurements do represent an approach to the critical point, over the full range of temperatures reported. The opalescence measurements are considered crucial to the conclusions drawn from the sound-absorption measurements.

Initially, as the temperature of the present critical mixture was lowered following the critical isochore in the homogeneous phase, the sound absorption showed the expected scaling behavior for critical slowing down. When within 2 or 3 K of T_c the singular behavior of this critical scaling began to vanish, and within 0.2 or 0.3 K of T_c the sound absorption had no measurable singular behavior, i.e., it remained constant. This measured result is at least qualitatively similar in some respects to the calculations of Harada *et al.*[1] using the Fixman-Kawasaki and scaling theories. Sound-absorption measurements very near the critical mixing point clearly do not obey the mode-mode coupling theory for the fluctuation-driven coupling of transport modes.

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