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Ultrasound absorption near the critical point of SO_2+CCl_4 liquid mixtures

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Ultrasonic absorption and velocity have been measured in several liquid mixtures of $SO_2 + CCl_4$. Special emphasis was given to the homogeneous-solution region near the critical mixing point. Near the critical point it was found that high absorption and strong frequency dependence were characteristic of the ultrasound, unlike its behavior outside of the critical region. The frequency dependence of the absorption measurements near the critical point and along the critical isochore can be satisfactorily fit with the Kawasaki multiple-relaxation calculation by the adjustment of three fit parameters. Near the critical point the background absorption was found to be independent of frequency over the range of investigation (2 to 66 MHz). Including an adjustable single-relaxation term in the absorption fit indicated that the best fit was obtained as the amplitude of the single-relaxation term went to zero. The characteristic-frequency and amplitude parameters, taken from fits of the Kawasaki calculation to the data nearest the critical point, were scaled in reduced temperature. The characteristic-frequency data are consistent with a scaling exponent of 1.89 ± 1 if a critical temperature is chosen for the scaling that is slightly lower than the observed phase separation temperature, i.e., if the presence of a pseudospinodal curve is assumed. This is the exponent value that is predicted by the mode-mode coupling and Ising lattice-gas theories. Neither dispersion nor temperature-dependent anomalies were observed for the ultrasonic velocity.

I. INTRODUCTION

The anomalous absorption of ultrasound near the critical point of one- and two-component fluids has been studied experimentally in numerous systems. In only a very few of these studies, however, have there been sufficient data to allow a comparison of the results with theoretical predictions for transport properties near the critical point.[1-4] Further, a clear and unambiguous comparison with critical-point theory for some of these systems that have been studied experimentally has been made much more difficult by the presence of temperature- and sound-frequency-dependent background effects.[1]

Near the critical mixing point in binary liquid mixtures the presence of concentration fluctuations greatly increases the absorption of sound in the low-MHz range. It has been suggested that the fluctuations are responsible for a mode-mode coupling between the various transport modes of the fluid mixture.[5] In binary mixtures the sound absorption is increasingly coupled to the mass-diffusion mode as the critical point is approached. Fixman,[2] and later Mistura[6] have suggested that a relaxing complex heat capacity coupled to the mass-diffusion mode via the concentration fluctuations would provide a multiple-relaxation absorption of the sound. Kawasaki[7] has made a similar suggestion in terms of a relaxing complex viscosity. In both of these calculations, the diffusive decay of concentration fluctuations determines the single fundamental relaxation rate for sound absorption. If D is the diffusion coefficient for the fluctuations then the fundamental relaxation frequency is $f_D = D/\pi\xi^2$, where ξ is the fluctuation correlation length. In these calculations the fluctuations are assumed to have a pair correlation function of the Ornstein-Zernike type. It is noted that the form of the pair correlation function only changes the outcome of these calculations when the sound frequency f is at least one order of magnitude greater than f_D.

For both forms of the calculation the excess absorption due to the critical fluctuations is expressed in terms of a reduced frequency $f^* = f/f_D$ and has the form

$$\alpha/f^2 = [2\pi A(T)/u_0 f_D]F(f^*)\,, \tag{1}$$

where u_0 is the low-frequency sound velocity, $A(T)$ is a dimensionless amplitude, and $F(f^*)$ is the integral

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

and $x = k\xi$, for k the fluctuation wave number. The function $K(x)$ was taken by Kawasaki to be $K(x) = \frac{3}{4}[1 + x^2 + (x^3 - x^{-1})\arctan x]$. The dimensionless amplitude in Eq. (1) is given by, in terms of various thermodynamic quantities, as

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

where k_B is Boltzmann's constant, ρ is the density, C_v is the specific heat at constant volume, P is the pressure, and T is the absolute temperature. Both theories also predict the sound dispersion caused by the critical fluctuations, and their calculations give somewhat different results.

These multiple-relaxation calculations have been generally successful in predicting the frequency dependence of the ultrasonic absorption near one- and two-fluid critical points. Very little dispersion, if any, is usally observed near a binary-mixture critical point, and it is not yet clear which form of the multiple-relaxation calculation will best describe the sound-velocity anomaly.[1]

Mode-mode coupling theory of transport phenomena near critical points in binary mixtures[5] also predicts that the mass diffusion scales as $D \simeq \xi^{-1}$. Calculations based on the Ising lattice gas predict that the correlation length scales as $\xi \sim \epsilon^{-\nu}$ for an exponent $\nu \approx 0.630$ and $\epsilon = (T - T_c)/T_c$. Taken together they predict the scaling exponent for D and hence for f_D. In the latter case the exponent is predicted to be about 1.89 in binary liquid mixtures with the requisite symmetry and short-range forces to put them in the Ising lattice-gas universality class.[4] This value for the scaling exponent has been shown to be consistent with some of those measurements of sound absorption in binary mixtures[1,2,6] where the data quality allowed a determination of the temperature dependence of f_D.

An alternate suggestion has been made recently concerning the significance of the scaling of sound absorption and the characteristic frequency.[8] This model proposes that the sound is absorbed by an acoustic resonance of microscopic droplets in the fluid near its critical point. A very simple physical model of the droplet resonant modes is able to provide a scaling exponent and amplitude in fair agreement with the observed values for xenon near its liquid-gas critical point. The model is not, however, refined enough for our use here.

Of course, in any real system the measured sound absorption will have contributions due to processes in the liquid other than just the critical fluctuations.[9] The Navier-Stokes classical absorption, due to the nonrelaxing viscosity and thermal conductivity of the liquid, will make a frequency-independent contribution to the measurement of α/f^2 in all liquids. Also, many liquids undergo one or more single relaxations as a consequence of thermal or structural rate-dependent processes in the liquid. These so-called single-relaxation processes do contribute a frequency-dependent absorption to α/f^2. Typically then, the observed absorption of sound near a binary-liquid critical point is a sum of three or more terms of the form

$$\alpha/f^2 = R_{\text{CPMR}} + \sum R_{\text{SR}} + R_{\text{NS}} \ , \tag{4}$$

where R_{CPMR} is the critical-point multiple-relaxation term given in Eq. (1), R_{SR} refers to single-relaxation terms of which there may be several, and R_{NS} refers to the Navier-Stokes term which can be expressed as $B(T)$, a frequency-independent quantity often small compared to the overall absorption. If the sound frequencies in a particular set of measurements are very much lower than the single-relaxation frequency for some process, then the corresponding contribution to α/f^2 is frequency independent and can be included in $B(T)$.

We have chosen to study absorption in the binary liquid mixture $SO_2 + CCl_4$ for several reasons. Most importantly, the physical and chemical nature of the mixtures is anticipated to be fairly simple, outside of the cooperative effects leading to phase separation. In particular, there should be no difficulty with chemical complexes, hydrogen bonding, or acid-base reactions that are well known to contribute strong single-relaxation terms to the measured sound absorption.[1,9] Also, the sound-absorption properties of pure liquid CCl_4 are known to be frequency independent below about 100 MHz, and the properties of SO_2 in the low-MHz range have also been thoroughly studied. In a recent paper we report sound absorption measurements in pure liquid SO_2 in the same temperature range as the present measurements.[10] The observed single-relaxation frequency in liquid SO_2 was temperature independent and unaffected by the addition of a small amount of cyclohexane impurity. The single-relaxation amplitude, however, did tend to vanish rapidly with the addition of impurity in that system.

The coexistence curve for phase separation in liquid mixtures of $SO_2 + CCl_4$ was first investigated by Bond and Beach.[11] They have determined the critical temperature T_c to be 243.9 K, however, their phase-separation temperatures were measured by a visual method as the temperature was slowly being raised, and may therefore differ somewhat from determinations made under equilibrium circumstances. We have estimated the critical concentration X_c from their phase-coexistence data to be 0.58 ± 0.02 weight fraction CCl_4, where the uncertainty is due to the rather few data points available.

II. EXPERIMENTAL METHOD

The measurements presented here were made with an ultrasonic pulsed spectrometer described in detail elsewhere.[4,12] The usual variable-path-length design with two transducers was used. The sound was generated in an upper transducer whereupon it passed downward through a fused-silica delay line, through about 1 cm of liquid sample, into a short lower Pyrex-glass delay line, and finally into a receiving transducer. The upper delay line and transducer could be translated vertically by a stepping motor in steps of no less than about 10^{-3} mm, and a stainless-steel bellows was used to seal the movable delay line to the glass sample cell. About 50 cm^3 of liquid sample was typically placed in the cell, giving the sample a depth of about 2 cm, the lower portion of which was used for the acoustic measurements. The temperature of the sample was regulated within ±0.02 K by a large stirred alcohol bath, and was measured by a platinum thermometer calibrated within ±0.1 K and repeatable within a few millidegrees.

A fully automated system was used to generate, receive, and analyze the ultrasound pulses. This system is described in detail elsewhere.[4,12] Our measurements of the absorption of sound reported here were made with a precision of about ±5%, except at 2 MHz, where the precision was ±10%. Noticeable diffraction of the acoustic beam occured at 2 MHz and was corrected for in the automated data analysis.[13] Data in the range of 2 to 26 MHz were obtained with a matched pair of 2-MHz-fundamental crystals, while data in the range of 28 to 66 MHz were obtained with a matched pair of nominally 10-MHz-fundamental crystals. This necessitated two separate experimental runs that were carried out under nearly identical circumstances. Various standards were used to calibrate the spectrometer over the full usuable-frequency range and ensured that two data sets agreed within the precision reported above.

Spectroscopic-grade CCl_4 was used without further purification in sample preparation. Anhydrous-grade SO_2 gas supplied by the Matheson Company[14] was dried and purified by both a phosphorus-pentoxide trap and a dry-ice cooled trap. After cleaning, the gas was evaporated into a volumetric flask and then condensed into the sample cell.

III. RESULTS AND ANALYSIS

We have investigated the temperature and frequency dependence of the ultrasonic absorption and velocity for six different mixtures of $SO_2 + CCl_4$ with the following concentrations: $X = 0.470$, 0.585, 0.647, 0.783, 0.870, and 0.945 (X is weight fraction CCl_4). For each sample, data were gathered from 263 K down to the temperature where the phase separation was first observed to occur. The phase-separation temperatures we observed were consistent with the general shape of the coexistence curve mapped by Bond and Beach,[11] but displaced downwards in temperature by about 1.5 degrees. Our observations of the coexistence curve were all equilibrium measurements, the temperature being changed in increments only, after a wait of several hours, typically, near the phase separation. Upon phase separation the new phase was initially cloudy, but later it became transparent as equilibrium was established. We have few points locating the coexistence curve near the critical concentration, thus we have taken for X_c the value most consistent with the data of Bond and Beach, and find no discrepancy with our data in this choice. One of our six samples, the one with $X = 0.585$, is undoubtedly within about ±0.02 of the critical value, as was estimated from visual checks of the meniscus height in the mixtures just after phase separation was first observed.

The coexistence curve we have found is shown by the dashed line in Fig. 1. Also in the figure are ultrasonic absorption measurements, shown as α/f^2, taken at 10 MHz in the six mixtures all at the same temperature: 243.2 K. This temperature is about one degree above the observed phase separation temperature for the $X = 0.585$ mixture. The smooth line drawn through the absorption data in Fig. 1 indicates the extent of the absorption peak associated with the critical point. The rise in sound absorption seen at high CCl_4 concentrations is undoubtedly due to the approaching limit of pure CCl_4. The relatively high absorption of pure CCl_4 is a consequence of a relaxation process occuring at a frequency well above that relevant to the present measurements. Our earlier measurements in

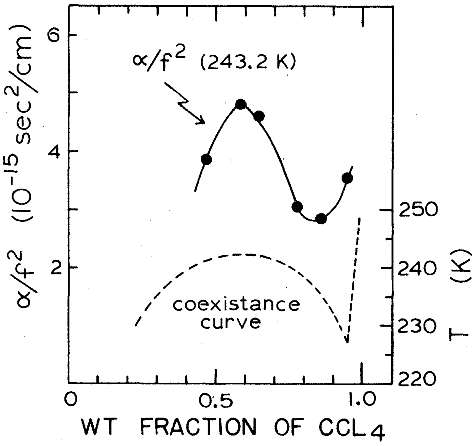

FIG. 1. Phase coexistence curve for $CCl_4 + SO_2$ mixtures, and the measured ultrasonic absorption along the 243.2-K isotherm in these mixtures. The absorption measurements shown are those for 10-MHz sound. The solid line through the absorption data points is a visual aid only. The dashed line represents the coexistence curve taken from smoothed data combined from our data and the data of Bond and Beach (Ref. 11). The latter data have been shifted downward about 1.5 K for the purposes of constructing the figure, as explained in the text.

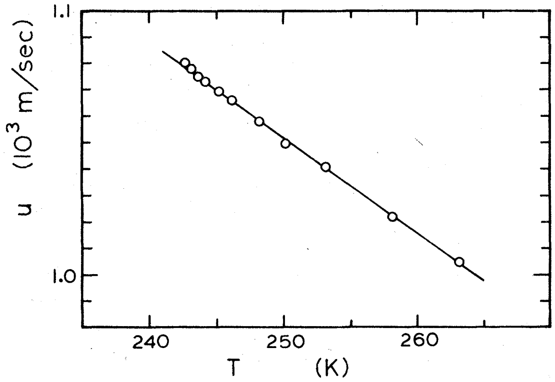

FIG. 2. Velocity of ultrasound as measured in an $X = 0.585$ mixture at 5.8 MHz. The solid line is a linear least-squares fit to the data.

pure SO_2 in this temperature range indicate that the 10-MHz absorption for $X = 0$ would be slightly higher than the absorption peak shown in the figure for $X = 0.585$. Thus it appears that in the absence of a nearby critical point the acoustic absorption in $SO_2 + CCl_4$ mixtures would be well below that of either of the pure components.

The ultrasonic velocity observed in the homogeneous mixtures was a linearly decreasing function of temperature for all the mixtures investigated. In Fig. 2 are shown representative velocities of sound data, in this case for the $X = 0.585$ mixture. No dispersion was ever observed in these mixtures within the ±0.2% precision of the instrument. Thus, the data shown in Fig. 2 can be taken as the low-frequency-sound velocity even though it was in fact measured at 5.8 MHz. The velocity data at each concentration can be satisfactorily fit to a linear function: $u = aT + b$. In Table I are shown the values of the coefficients a and b taken from least-squares fits to the velocity data in the $X = 0.470$, 0.585, and 0.647 mixtures. It is seen that $-a$ and b are increasing functions of X.

Our measurements show that α/f^2 was frequency independent away from the critical region, where the absorption can be considered to be only the background portion. The background absorption was somewhat large, however, and had a slight

TABLE I. Calculated values for the slope and intercept of a linear least-squares fit to the velocity data at three concentrations in $SO_2 + CCl_4$ mixtures.

Concentration X	Slope a (m/sec K)	Intercept b (m/sec)
0.470	−3.30 ± 0.1	1879 ± 10
0.585	−3.51	1929
0.647	−3.87	2017

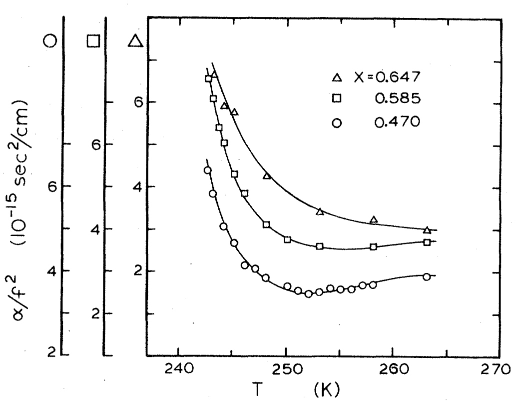

FIG. 3. Absorption of 5.8-MHz ultrasound in three mixtures at various temperatures. The three mixture concentrations are tabulated in the figure. The mixture $X = 0.585$ is near the critical value. The solid lines drawn through the data are visual aids only.

temperature dependence as is evident in Fig. 3. The figure shows the sound absorption at 5.8 MHz for the three mixtures nearest the critical value. Because of the strength of the background absorption, the critical region is limited to about 6 degrees above T_c along the critical isochore, as can be seen from the $X = 0.585$ curve in Fig. 3.

Near the critical point the sound absorption showed considerable frequency dependence. We have fit the frequency dependence of the absorption with Eq. (4) and found that the best fit was obtained as the single-relaxation amplitude tended to zero. Hence, data along the $X = 0.585$ isochore were fitted by Eq. (1), the critical absorption, plus a constant background term $B(T)$. Thus, the fits reported here were made with a total of three adjustable parameters: f_D, $A(T)$, and $B(T)$. Absorption data very near the critical point are shown in Fig. 4 along with the best fit of Eq. (1) as just described. These multiple-relaxation fits are accomplished by successively recalculating the integral $F(f^*)$ and then testing Eq. (1) against the data for various choices of the adjustable parameters. No explicit weighting was given to the data, but as is evident in Fig. 4, these mixtures absorbed much more strongly at the lower frequencies available in our measurements, and so these lower-frequency data more strongly determined the best choice of $A(T)$ and f_D than did the higher-frequency points. Unfortunately, the uncertainties that arise in the diffraction corrections of the 2-MHz data points leave this data somewhat less reliable than the higher-frequency data, and hence limit the precision of our determinations of $A(T)$ and f_D. This is especially true for the smaller values of $A(T)$, which were found away from the critical point.

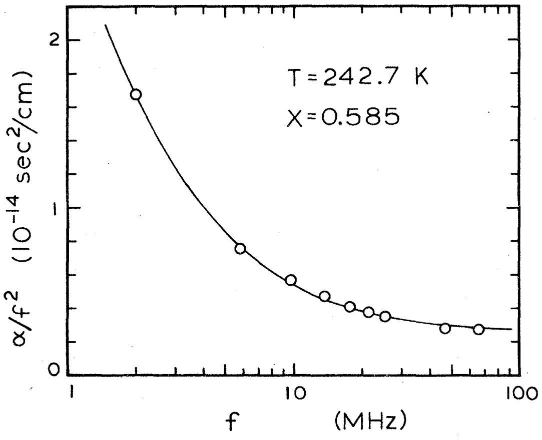

FIG. 4. Frequency dependence of the ultrasonic absorption in a mixture near the critical point. The solid line represents a least-squares fit of the Kawasaki calculation to the data.

When absorption data admit to a satisfactory fit involving only a CPMR term and a frequency independent $B(T)$ term it is possible to express the absorption per wavelength, $\alpha\lambda$, as a reduced quantity that only depends on f^* and no longer on T. Such a reduced $\alpha\lambda$ is written as

$$(\alpha\lambda)^* = \frac{(\alpha/f^2) - B(T)}{2\pi A(T)} u_0 f_D = F(f^*) . \qquad (5)$$

Following this scheme, our data for the $X = 0.585$ mixtures are shown in Fig. 5 where they can be compared with the integral $F(f^*)$, the solid line, obtained from the Kawasaki calculation. Figure 5, then, represents a collection of data sets, for $X = 0.585$, each of which has been fit as in Fig. 4.

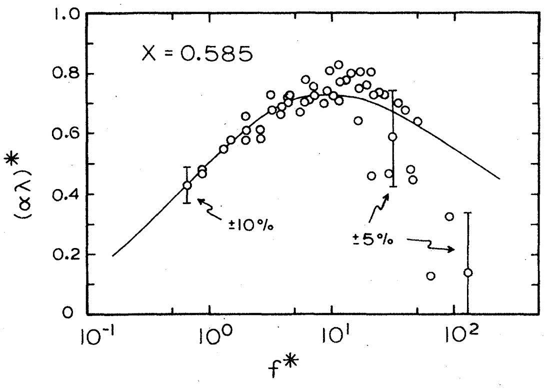

FIG. 5. Reduced absorption per wavelength at various reduced frequencies for the mixture with $X = 0.585$, a value near the critical isochore. The data shown are from 242.7 to 246.2 K. The experimental uncertainties shown refer to uncertainties in the measurement of α/f^2, and are discussed in the text. The solid line represents the Kawasaki calculation.

It is evident in Fig. 5 that the data from the present study are satisfactorily described by the Kawasaki calculation. However, it is apparent that the fit for larger values of f^* is less successful, which may just be residual instrumental errors left from the procedure of combining the data sets of the 2- and 10-MHz crystals. We have indicated in the figure error bars of two types. The bar at ±10% uncertainty is for a datum point at $f = 2$ MHz, and the bars at ±5% are for $f = 66$-MHz data. Due to the dependence of F on f^* the 5% bars at 66 MHz are much larger in $(\alpha\lambda)^*$ space than are the 10% bars at 2 MHz. This clearly makes it much more difficult to test the success of the Kawasaki calculation with our data at larger values of f^*.

Recently there has been some interest in the nonhydrodynamic region where $f \gg f_D$ or $f^* \gg 1$.[3,4,15] In systems where the dispersion has been observed to be appreciable, the sound absorption in the nonhydrodynamic region did not follow either the Kawasaki or Mistura calculations. Clearly the present data can make no contribution to resolving this difficulty.

In order to test those scaling arguments discussed in Sec. I, we have fit $f_D(T)$ for the $X = 0.585$ mixture to the scaling relationship $f_D \sim \epsilon^{3\nu}$, or equivalently $f_D = f_{D0}\epsilon^{3\nu}$. These fits were made with three adjustable parameters: ν, T_c, and f_{D0}. Also, the number of data points was limited to only those nearest T_c where the CPMR term was sufficiently large compared to the $B(T)$ term that meaningful values of f_D could be obtained. As can be seen in Fig. 3, only the six or seven points nearest T_c are likely to be useful in a scaling analysis. The statistical success of our scaling fits to f_D has indicated that for these data only the six nearest points are useful, and these are the ones shown in Fig. 6.

The statistical χ^2 minimum is rather shallow as a function of T_c for the data points shown in Fig. 6(a). The value 241.2 K does, however, appear to be the best value of T_c for the present data, and has been used to construct the figure. The estimated uncertainty in this choice of T_c is about ±1 degree. It is important to note here that this choice of T_c for the sake of scaling experimental data does not imply that it is also the best choice for the true critical-point temperature or even that it should agree very closely with an observed phase separation temperature for a mixture with $X \approx X_c$. For our $X = 0.585$ mixture, phase separation was observed to occur at 242.4 ± 0.2 K which is somewhat above the scaling T_c calculated from the data. Although we have not measured its location anywhere except at $X = 0.585$, it appears that the $SO_2 + CCl_4$ mixture have a pseudospinodal curve

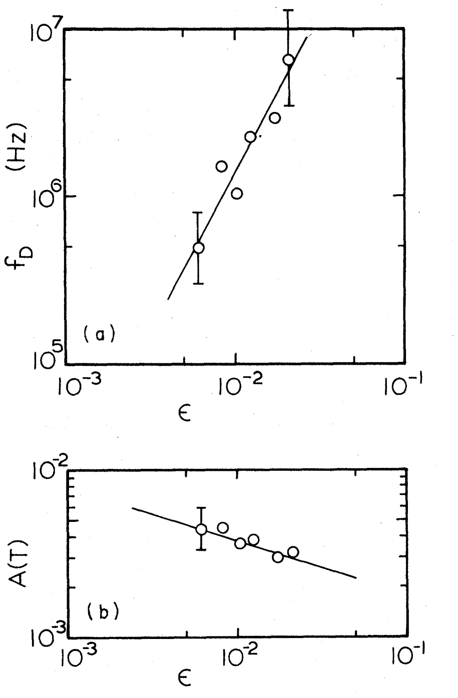

FIG. 6. Scaling in the critical region for the $X = 0.585$ mixture. (a) The characteristic frequency, f_D, as obtained from the fits to the Kawasaki calculation at various reduced temperatures ϵ. For the purposes of scaling, T_c was chosen to be 241.2 K. Representative error bars are shown indicating that the absolute uncertainty of the data near the critical point is somewhat better than that away from this region. The solid line is a least-squares fit to the scaling relation with a slope of 1.89 ± 1. (b) The multiple-relaxation amplitude $A(T)$ at various reduced temperatures. The same T_c was chosen here as in (a) above. The solid line is a fit of the scaling relation to the data, and it has a slope of -0.35 ± 0.2.

or locus of phase separation points inside the observed limit of stability of the homogeneous solutions. Light-scattering measurements near a binary-liquid-mixture critical point[16] have shown that the concept of a pseudospinodal curve may be quite useful. This concept allows the scaling of experimental data toward a separation point that is never actually realized; but, significantly, the exponent is then the same as that which would be measured in an experiment where the separation point could be approached arbitrarily closely.

Since our data for the $X = 0.585$ mixture do not cover a particularly wide range in reduced temperature, and since the f_D quantities have not been determined to a high precision, for reasons discussed in Secs. II and III, the scaling of our data has not yielded a particularly well-defined value of the scaling exponent ν. The scaling of the f_D data in Fig. 6(a) with $T_c = 241.2$ K has the exponent 1.89 ± 1 or $\nu = 0.63 \pm 0.3$, where the exponent uncertainties reported are about three standard deviations of the fit to the data. Thus, we feel that our data are consistent with the value of ν calculated from the Ising lattice gas (0.630), if not a particularly stringent test of that value. Clearly the scaling exponent for f_D, that was measured here, represents the scaling of a transport property of the liquid, which may in general not be even as universal as the scaling exponents of static properties.[17] There is, however, little data available to check for universality in transport properties and it was one of the aims of the present work to make a contribution here.

We have also estimated the scaling exponent for the CPMR amplitude $A(T)$ under the same circumstances as for f_D. In Fig. 6(b) are shown the six data scaled with the same scaling temperature T_c and having an exponent value -0.35 ± 0.2, where again the indicated uncertainty is three standard deviations of the fit. An analysis of the various quantities in Eq. 3 that contribute to $A(T)$ shows that only ξ is usually singular in binary mixtures, so that $A(T)$ should scale as $A(T) \sim \epsilon^{3\nu - 2}$. From the Josephson scaling inequality[18] $3\nu - 2 \geq -\alpha$, and the Ising lattice-gas value for the exponent $\alpha \approx 0.110$, we see that $A(T)$ should scale as $A(T) \simeq \epsilon^{-a}$ for $a \geq 0.110$. The exponent we have measured satisfies this inequality but not the equality. Under the circumstances we do not consider the latter fact significant.

The observation that the present data are consistent with Ising lattice-gas exponents for static-system calculations is surprising if one recalls the factors determining universality classes. In addition to dimensionality, the symmetry and interaction range of a critical system should determine the universality class it falls into.[18] In the present situation we are dealing with a mixture, one component of which is a polar molecule, and hence without the requisite symmetry and short-range interaction to categorize it with the usual liquid-gas and binary-mixture universality class. The dipolar interactions of the SO_2 molecules are relatively long-range interactions. For a sufficiently long range the Ising lattice-gas behavior should not occur, but rather a mean-field type of behavior should characterize the critical-point scaling. It is not yet clear why it should be,[19] but there is some limited experimental evidence that polar fluids, under the usual experimental circumstances, scale as if they were rotationally symmetric with short-range forces. It is, of course, possible that the $SO_2 + CCl_4$ mixtures are in fact not scaling with Ising lattice-gas exponents but with nearby values, which the precision of our measurements has precluded detecting.

IV. CONCLUSIONS

The critical mixing point in $SO_2 + CCl_4$ mixtures has provided fruitful terrain for an ultrasonic study. The nature of the background absorption, that which is not caused by critical-point effects, is a crucial factor in the practical execution of such experimental measurements. Fortunately, the $SO_2 + CCl_4$ mixtures had a frequency-independent background in the region of our studies. However, the background was not small enough, compared to the strength of the critical absorption, so as to allow a particularly wide temperature range within which to investigate the critical effects.

The absence of dispersion or temperature-dependent anomalies in the measured sound velocity is certainly consistent with findings in other binary mixtures. Near the critical point the excess sound absorption could be described quite satisfactorily by a multiple-relaxation calculation of the Kawasaki type, where a single characteristic frequency is sufficient. The usefulness of such an analysis lies in its reduction of a large quantity of data with several variables into a single quantity and its temperature dependence. Furthermore, this characteristic frequency is just the diffusive decay rate for fluctuations, which can be compared straightforwardly with theoretical predictions, i.e., scaling, for the critical behavior of diffusion. Under such an analysis, the data reported in the present study was shown to be consistent with the scaling predicted by the mode-mode coupling and Ising lattice-gas theories. Since SO_2 is a polar molecule without rotational symmetry and with long-range dipolar interactions, it is not immediately apparent why its scaling behavior should be consistent with that expected for an Ising lattice gas where symmetry and short-range forces are important.

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