

FIGURE 6. Plot of $\ln(D\rho)$ versus $\ln T$. The points below 0 °C are based on the smooth curve drawn through the diffusion constant data of reference 17.

errors, while the measurements of ρ_l/ρ_v are accurate to ± 2 percent.

Interpretation: Experiments performed at 32 and 40 °C in noncritically loaded samples showed that $D \propto \rho^{-1}$ in the range $\rho_c/2 < \rho < 2\rho_c$. Thus $D\rho$ is a function of temperature only in this density range far from the critical point. A plot of $\ln(D\rho)$ versus $\ln T$ from just above the melting point at 89.9 to 333 °K approximately 30 °K above the critical point, is shown in figure 6. The results of Gaven, Stockmayer, and Waugh [17] far from the critical point are included. The resulting straight line gives $D\rho \propto T^{2.9 \pm 0.1}$. This is an empirical relationship which does not necessarily hold for other substances. Figure 7 gives a plot of $D\rho$ versus T in the temperature region within a few degrees of T_c . A comparison with the results of figure 6, as given by the solid line of figure 7, shows that $D\rho$ goes through a pronounced minimum for the liquid near T_c with its minimum value about 20 percent below the solid line. A similar but smaller effect is observed for the vapor but, unlike the data for the liquid, we cannot say definitely that the vapor minimum is not due to a systematic error, which we estimate to be less than 5 percent. A single measurement of D for a pure sample at 24 °C, having an error of ± 10 percent agrees with D for the impure sample.

The interpretation which we propose for the data

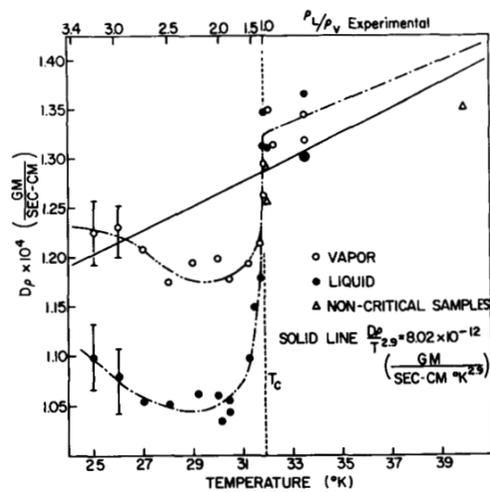


FIGURE 7. Plot of $D\rho$ versus temperature near T_c . Measured values of ρ_l/ρ_v are also shown. The samples used were loaded to the critical density. Measurements of $D\rho$ based on the slopes of $1/D$ versus ρ plots at 32 and 40 °C, using noncritically loaded samples are also shown. The dotted line at 31.9 °C labeled T_c is an upper limit for the critical temperature since it is the lowest temperature at which $\rho_l/\rho_v = 1$, within experimental error.

of figures 6 and 7 is that whereas, for systems not too close to the region of the critical point $D\rho$ is a function of temperature only, the diffusion constant decreases anomalously near the critical point.

In figures 6 and 7, T_c for the impure sample used has been nominally given as 31.9 °C as compared with 32.32 °K. This actually represents an upper limit for T_c since it is the temperature at which $\rho_l/\rho_v = 1.0$ within experimental error. Since we do not know the equation of state for the impure sample, we cannot take into account the influence of gravity in a reliable fashion, but an examination of figure 3 indicates that the true value of T_c (or region of T_c) is probably close to the temperature at which $D\rho$ goes through its minimum value.

As far as we know these are the first measurements of a self diffusion constant near the critical point. Dr. B. Jacrot has, however, drawn our attention to some published measurements of the diffusion constant of Iodine in CO_2 near the critical point [18], where it is found that the diffusion constant is practically zero. This is consistent with the anomalous decrease observed by Noble for $D\rho$ for ethane near T_c as shown by figures 6 and 7. Obviously, it would be desirable to make further measurements of D near the critical point for samples having better geometry (flat, horizontal samples) and a higher degree of purity, e.g., SF_6 would be a good system to study since the relaxation time T_1 of pure SF_6 is reasonably short [11].

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Ultrasonic Investigation of Fluid System in the Neighborhood of Critical Points

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1. Introduction

It is the intention of this paper to examine the research that has been so far carried out in fluid critical systems by means of sound waves. Since 1940 several authors have attempted to study the propagation of sound waves in order to find information on the nature and the behavior of these particular media: various indications and suggestions have been obtained, which have contributed to a better definition of the problems concerning critical systems. The solution of these problems is however far from complete.

The quantities which are usually measured are the velocity and the sound absorption coefficient; they may be determined as functions of temperature, frequency and, in the case of mixtures, of composition. It must be observed that the information available at present for the systems in which sound measurement have been performed, is only partial because it usually refers to only one of these quantities (i.e., velocity or absorption coefficient) determined in a limited range of one of the variables, temperature, frequency, and composition.

Strong similarities exist between liquid-vapor and liquid-liquid critical systems as well as some dissimilarities. It is preferable for a clearer exposition to review separately the work made on each of the two types of systems, though this

procedure will require some repetition. We consider first the case of liquid-vapor critical media.

2. Liquid-Vapor Critical Systems

Table I, although it is not complete,¹ indicates the substances which have been the object of the more extensive experiments. Together with pure liquids, few binary or ternary mixtures have been investigated in the liquid-vapor critical region. The experiments have been performed either at a single frequency or in a rather limited frequency range. Moreover velocity and absorption coefficient determinations have usually not been made on the same system.

Figure 1 gives the results of Tielsch and Tanneberger [5] for the sound velocity in gaseous CO_2 as a function of pressure at constant temperature. In the examined frequency range (0.4-1.2 Mc/s) and in the limits of error (0.2%) no dispersion has been found. The same conclusion was reached by Parbrook and Richardson [3] in the range 0.5-2 Mc/s. The velocity goes through a minimum which becomes sharper and sharper as the temperature approaches the critical one: the minimum velocity

¹ In particular much research of Russian authors is included in thesis not easily available; some results are reported in quotation [9].

TABLE I. Sound Propagation in Liquids-Vapor Critical Systems

Substance	T_c	P_c	Temperature	Pressure	Frequency	Quantity measured	Author
Helium	5.1994 °K	1718 mm Hg	$T_c - 0.03$ $T_c + 0.04$ °K	$p - 40$ $p_c - 35$ mm Hg	1 Mc/s	c	Chase-Williamson-Tisza [1].
Xenon	16.74 °C	58.2 atm	15-19 °C	0.25-1.25	c, α	Chynoweth-Schneider [2].
Carbon dioxide	31.4 °C	.73 atm	19-38 °C	up to 100 atm	0.5-2	c, α	Parbrook-Richardson [3].
			28-38 °C 25-48 °C	5-98 atm 35-120 atm	0.270 0.410	c, α c, α	Herget [4]. Tielsch-Tannaberger [5].
Ethylene	9.7 °C	50.9 atm	7-18.7 °C	up to 100 atm	0.5-2	c, α	Parbrook-Richardson [3].
Hydrogen chloride	51.4 °C	81.6 atm	9.7-23 °C 38-62 °C	35-75 atm	0.27-0.6	c	Herget [4].
N ₂ O Nitrous oxide	36.5 °C	71.7	52-62 °C 32-37 °C	55-150 atm	1.9 1-9	c α	Breazeale [6]. Noury [7].
n-hexane	234.8	29.5 atm	along the saturation curve	2-3	c	Nozdrev [8].
n-heptane	266.8 °C	26.8 atm	along the saturation curve	2-3	c	Nozdrev.
Methyl acetate	233.7 °C	46.3 atm	along the saturation curve	2-3	c	Nozdrev.
Ethyl acetate	250 °C	37.8 atm	along the saturation curve	5-13	c	Kal'ianov [10].
					2-3 5-9	c c	Nozdrev [9]. Nozdrev [8].
Propyl acetate	276.2 °C	32.9 atm	along the saturation curve	2-3	c	Nozdrev [8].
Methyl alcohol	240-240.5	78.7 atm	along the saturation curve	2-3	c	Nozdrev.
Ethyl alcohol	243.1	63.1 atm	along the saturation curve	2-3	c	Nozdrev.
Isobutyl alcohol	283.4	along the saturation curve	2-3	c	Nozdrev.
Sulphur hexafluoride	45.6 °C	36 atm	0.6	c, α	Schneider [12].
Water	374 °C	217.5 atm,	along the saturation curve	2	c	Nozdrev-Osadchii-Rubtsov [13].
Benzene methyl alcohol	239 °C for 10% benzene	along the saturation curve	c	Nozdrev-Taraitova [14].
Benzene methyl-alcohol-toluene	240-320 °C	along the saturation curve	c	Grechkin-Nozdrev [15].

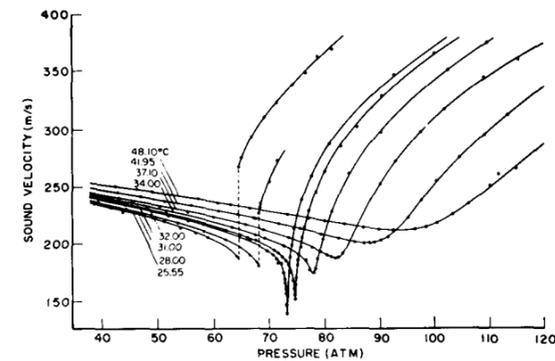


FIGURE 1. Sound velocity in CO₂ versus pressure, at constant temperature (H. Tielsch and H. Tanneberger [5]).

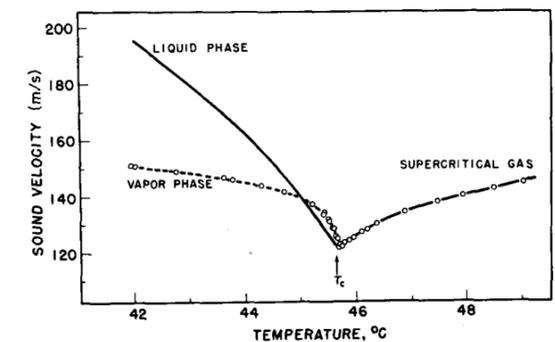


FIGURE 2. Sound velocity for the liquid and the vapor phase of sulfur hexafluoride (W. G. Schneider [12]).

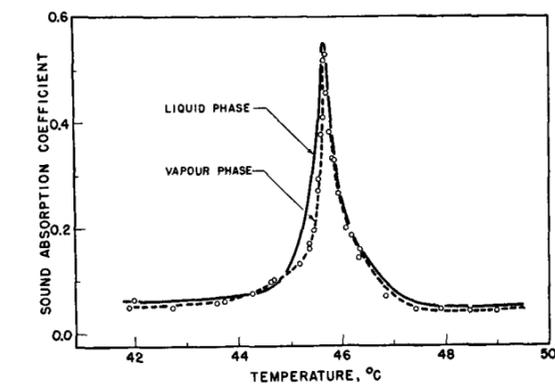


FIGURE 3. Sound absorption for the liquid and the vapor phase of sulfur hexafluoride (W. G. Schneider [12]).

measured at 31 °C is about one half of the value in normal conditions.

Figures 2 and 3 give Schneider's results (600 kc/s) on velocity and absorption in sulfur hexafluoride, a nonpolar compound with spherically symmetric molecules [12]; the data are in this case available for the liquid phase as well as for the vapor on both sides of critical temperature (T_c).² The velocity in the liquid and in the gas seems, in the limits of experimental errors, to reach a common minimum at a temperature which coincides with T_c ; the absorption coefficient in both phases increases very rapidly approaching T_c .³ The last circumstance has been observed in all systems examined and the various researchers have not succeeded in making a measurement at T_c .

Figures 4 and 5 give the results of Chynoweth and Schneider in xenon [2]. The absorption coefficient was measured at 250 kc/s and it shows a behavior similar to that observed in sulfur hexafluoride when T approaches T_c . The velocity instead was measured in the range 250 kc/s-1,250 Mc/s: a dispersion has been detected whose magnitude is largely higher than the experimental error (0.2-0.7%). We will discuss the inferences of this result shortly. At present we call attention to the fact that Chynoweth and Schneider have not noticed any tendency of velocity towards a discontinuity or a sudden drop to zero when T approaches T_c . Until recently, this has been a general conclusion of experiments. Nozdrev [8], for instance, who has made velocity measurements using light diffraction by sound waves, claims to have been able to visually follow the continuous change of sound velocity through the critical point.

The fact that the velocity of sound remains finite at the critical point is in agreement with standard thermodynamics [16]. In this state, the derivative of pressure respect to volume at constant temperature vanishes: $(\frac{\partial p}{\partial v})_T = 0$. Consequently, the specific heat at constant pressure (C_p) is infinite while C_v , the adiabatic compressibility and the sound velocity stay finite.

It may be of some interest, at this point, to mention some results that have been obtained by Nozdrev [8, 9] who has performed extensive velocity

² The full and broken lines above T_c in figure 3 correspond to measurements in the supercritical gas performed respectively near the sound source and far from it.

³ The velocity and absorption curves for liquid and vapor as obtained by Schneider cross at about 0.6 °C below T_c . This fact, which has no simple explanation, has not been found in any other case although some systems have been purposely investigated [8].

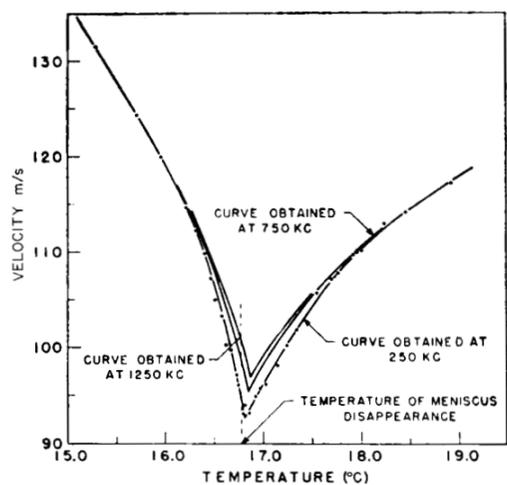


FIGURE 4. Sound velocity versus temperature in xenon (A. G. Chynoweth and W. G. Schneider [2]).

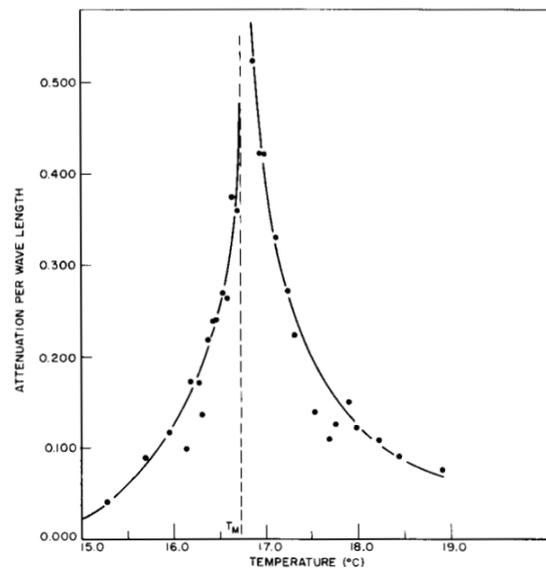


FIGURE 5. Absorption per wavelength ($\alpha \cdot \lambda$) versus temperature in xenon (A. G. Chynoweth and W. G. Schneider [2]).

measurement in critical fluids along the saturation curve. He has found, in the limits of error of his instrument, that the velocity variation along the saturation curve in both vapor and liquid near the critical temperature can fairly well be expressed by using van der Waals equation of state in the case of organic unassociated substances. This conclusion is not true for the liquid phase of associated liquids (e.g., ethyl alcohol) which proves that

associations may persist up to the critical point. Moreover, in the absence of dispersion and in the limits of experimental errors, Nozdrev establishes an empirical simple relation between the arithmetical average of sound velocities in the gas (c_g) and in the liquid (c_l) and ($T - T_c$)

$$\frac{c_g + c_l}{2} = c_{cr} + a(T - T_c) \quad (1)$$

being c_{cr} the common velocity at T_c and a a constant. This relation would be valid in the range between T_c and a temperature 15 to 30 °C below.

The standard thermodynamical treatment of critical state from which the conclusion on C_p , C_v , and c have been deduced, derives from some assumptions on the behavior of thermodynamical functions near the critical point:⁴ in particular it is assumed that the thermodynamical quantities (as function of V and T) do not show mathematical singularities along the curve which limits the region in which the substance can not exist as a homogeneous phase either in stable or in metastable equilibrium. Only in such case the above-

mentioned limit curve is determined by $(\frac{\partial p}{\partial v})_T = 0$ at the critical point alone.

The truth of this treatment has been seriously questioned recently. Some experimental results on C_r in argon [17] and in oxygen [18] have been obtained which indicate a logarithmic temperature dependence of such a specific heat near the critical point. If this behavior remains unchanged up to the critical point, C_r and the adiabatic compressibility would be ∞ and $c = 0$ at $T = T_c$ [19].

To obtain further information, Chase, Williamson, and Tisza [1] have performed sound velocity measurements in helium much more carefully and precisely than used in previous investigation near the critical point. The temperature was regulated to $\pm 10^{-4}$ °K (instead of $\pm 2 \cdot 10^{-3}$ °K in Chynoweth and Schneider measurements in Xenon), the pressure to ± 0.1 mm Hg; the velocity measurements were performed with a phase sensitive method having a resolution of 0.01 percent (the error in the Chynoweth-Schneider setup was $\pm 0.2 - 0.7\%$). Figure 6 gives the results obtained for the velocity both as a function of temperature (at a pressure $p = 1718 \pm 1$ mm Hg practically coinci-

⁴ Quotation [16] p. 262.

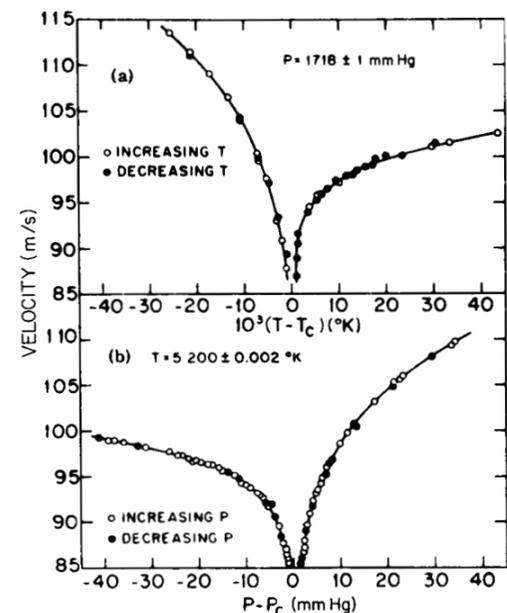


FIGURE 6. Sound velocity as a function of temperature (a) and pressure (b) in the critical region of helium (C. E. Chase, R. C. Williamson, and L. Tisza [1]).

dent with p_c) and as a function of pressure (at temperature 5.200 ± 0.0002 °K practically coincident with $T_c = 5.1994$ °K). The velocity decreases rapidly approaching the critical point. High absorption has not allowed measurements over a region of about $2 \cdot 10^{-3}$ °K or 2.5 mm Hg.

The fast decrease of c approaching the critical point in the range of temperature or pressure examined makes Chase, Williamson, and Tisza think the limit zero for c at T_c to be possible. The adiabatic compressibility K_S as a function at T or p has been calculated making suitable approximations for density: in the range examined, K_S seems to have a logarithmic singularity similar to that found for C_r in argon and oxygen.

This recent research, having questioned the standard thermodynamical treatment of critical states, opens a new exciting field of investigation. It must be observed, however, that the experimental results so far obtained, although they have caused serious doubts on the exactness of traditional thermodynamical treatment have not yet definitely proved it wrong. The measurement of c in helium for instance, shows a fast decrease of velocity when T approaches T_c , but at a separation of 10^{-3} °K from T_c the velocity has still a value quite different

from zero. The possibility of a leveling off at a much lower but finite value has not yet been excluded.

The behavior of velocity, C_r and adiabatic compressibility at the critical point remains a very interesting and exciting problem, which may clarify in depth the nature of systems in the critical state: it requires further experimental as well as theoretical research.

Closely related to the nature of liquid-vapor critical systems is also the enormous absorption that these media show. Two mechanisms have been proposed:⁵ scattering and relaxation.

A. G. Chynoweth and W. G. Schneider [2] have studied sound propagation in xenon in the hope of finding out which is the more important dissipative process. On the basis of an approximate calculation of scattering losses produced by inhomogeneities due to density fluctuations in the medium, they conclude that these losses do not appear sufficiently large to explain the experiment. They believe therefore that, as Schneider had already suggested in the case of sulfur hexafluoride, the more important dissipative mechanism is structural relaxation caused by sound-induced perturbation of equilibrium among molecular aggregates (clusters) present in the medium. The sound dispersion found in xenon (fig. 4) gives support to this explanation of high absorption. The relaxation phenomena would be characterized by a distribution of relaxation times.

Different conclusions were reached by H. D. Parbrook and E. G. Richardson [3] studying CO_2 and by M. A. Breazeale [6] in hydrogen chloride. The last author was unable to detect dispersion in the range 1 to 3 Mc/s; the absorption results could be interpreted as produced by relaxation processes with a wide distribution of relaxation times, but it seems also possible to explain them on the basis of a scattering mechanism if correlations between density fluctuations in adjacent volumes are taken into account. To evaluate the scattering losses, Breazeale, as already Chynoweth and Schneider had indicated, chooses the Libermann-Chernow [20, 21] formula, which was developed to deal with sound absorption caused by temperature inhomogeneities in the ocean. In the calculation of this formula the validity of an exponential autocorrela-

⁵ It seems that losses due to finite amplitude of waves cannot have importance, as experiments have shown that the signal detected by a sound receiver depends exponentially on the source-receiver distance.

tion function is assumed. The absorption coefficient due to scattering by inhomogeneities of diameter a is

$$\alpha_s = 8 \left(\frac{\Delta c}{c} \right)^2 \frac{k^4 a^3}{1 + 4a^2 k^2} \quad (2)$$

where $k = \frac{2\pi}{\lambda}$ and $\frac{\Delta c}{c}$ is the fractional change of sound velocity. In order to make a numerical calculation a was chosen 10^{-4} cm, i.e., approximately 10^3 molecular diameters as suggested by light scattering in various substances near the critical point; moreover, the value 0.25 was used for $\frac{\Delta c}{c}$. Figure 7 gives Breazeale's experimental results at various temperatures; the flags indicate the limits of errors. These results seem to depend upon the square of the frequency (dotted lines). The solid line on the same figure gives α_s calculated from (2) with above mentioned values of a and $\frac{\Delta c}{c}$; the correct order of magnitude of α is obtained; according to Breazeale the deviation of the experimental curves

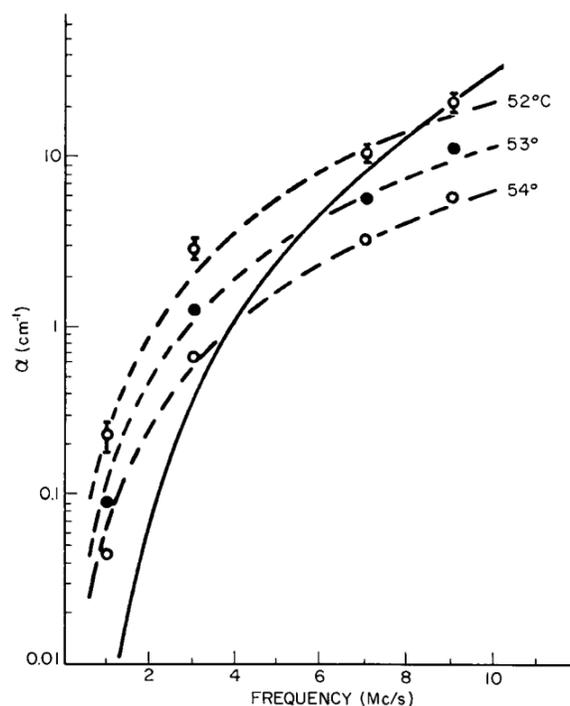


FIGURE 7. Absorption coefficient versus frequency at different temperature in the super critical region of hydrogen chloride (M. A. Breazeale [6]).

from the Libermann-Chernow curve, which essentially corresponds to a dependence of α from ν^4 , could be explained by using an adequate correlation between density fluctuations in neighboring volumes. Breazeale is therefore of the opinion that, while relaxation may be important at lower frequencies, scattering is most likely the main source of absorption in the range 1 to 9 Mc/s.

3. Mixtures of Partially Soluble Liquids

Table II indicates the few systems which have been studied in some way in the critical region of solubility. Almost all research has been limited in each system to only one mixture with a composition close to that of the maximum (or minimum) of the solubility curve.

Figure 8 is relative to a mixture having 47.6 wt percent of *n*-hexane in aniline [2]. The velocity was measured at 600 kc/s. The values of c in the two separate phases approach each other as T tends to T_c . On this basis, Chynoweth and Schneider formulated the tentative conclusions that the velocity in the three phases gradually tends to the same value as T approaches T_c and that no anomalous behavior is present. A different indication, however, emerges from the work of M. Cevolani and S. Petralia [23] in the aniline-cyclohexane mixture (49 wt % of cyclohexane) (fig. 9).

More research is needed to determine the exact behavior of velocity in the three phases in the immediate proximity of T_c ; the use of apparatus today available with smaller errors than those so far used in this kind of experiment should allow precise information.

No great effort, so far, has been made to investigate dispersion in the critical region of solubility and the few indications available [26] do not allow to reach any conclusion on the subject.

A common experimental finding is the high attenuation of sound waves in the critical region. Figure 10 [22] shows the typical behavior of the absorption coefficient per wavelength ($\alpha \cdot \lambda$) as a function of temperature through the critical region of solubility: it refers to the triethylamine-water system (44.6 wt % of amine) at 600 kc/s. Figure

11 [25] gives the parameter $\frac{\alpha}{\nu^2}$ for mixtures *n*-hexane-nitrobenzene as a function of composition;

TABLE II. Sound Propagation in Mixtures of Partially Soluble Liquids

System	Composition	T_c	Quantity measured	Temperature range	Frequency range	Author
Aniline <i>n</i> -hexane	47.6% w <i>n</i> -hex	68.3	c, α	55-74	0.6	Chynoweth-Schneider [22].
Aniline cyclohexane	51% w an.	c, α	15-55	3	Cevolani-Petralia [23].
Do.....	20-63% mole an	30.7	c, α scattering	29-34	1.5-5	Brown-Richardson [24].
Nitrobenzene <i>n</i> -hexane	0-100	21.02 °C	α	25	8	Sette [25].
	53.2 w% nitrob.	23.2	23-28	1-9	Alfrey-Schneider [24].
Water- triethyla- mine	44.6 w% am.	17.9	c, α	10-28	0.6	Chynoweth-Schneider [22].
	44.6 w% am.	α	15	7-54	Sette [25].
	34 w% am.	19.5	10-20	1-9	Alfrey-Schneider [24].
Water- phenol	34 w% Ph.	66	c, α	51-80	3	Cevolani-Petralia [23].

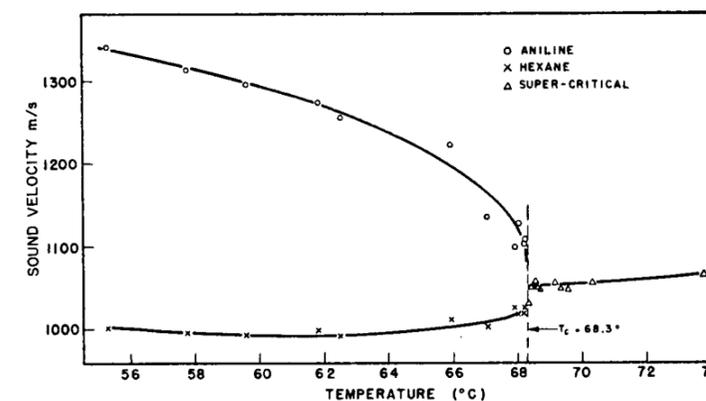


FIGURE 8. Sound velocity through the critical region of the aniline-hexane system (A. G. Chynoweth and W. G. Schneider [2]).

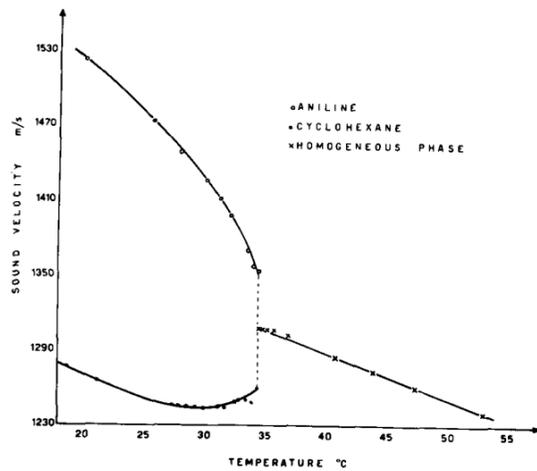


FIGURE 9. Sound velocity through the critical region of the aniline-cyclohexane system (M. Cevolani and S. Petralia [23]).

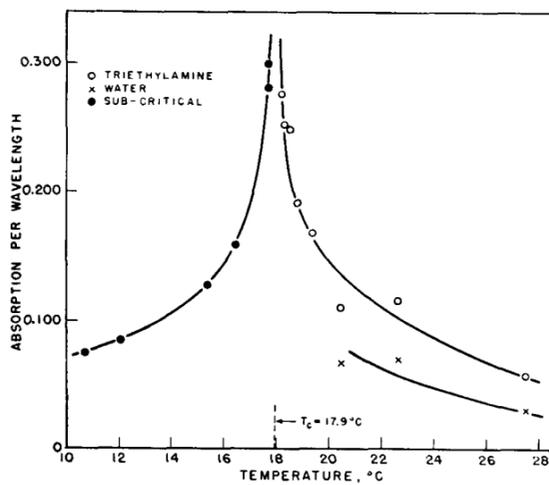


FIGURE 10. Sound absorption per wavelength ($\alpha \cdot \lambda$) versus temperature for the water-triethylamine system (A. G. Chynoweth and W. G. Schneider [22]).

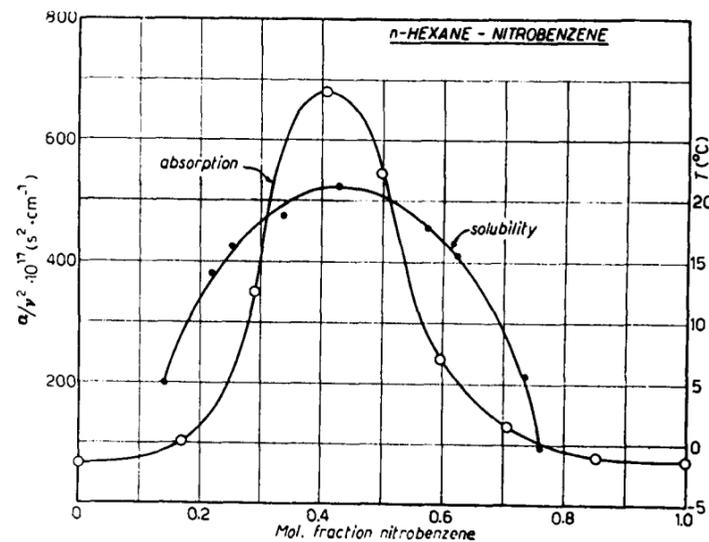


FIGURE 11. Sound absorption versus composition and coexistence curve for n-hexane-nitrobenzene mixtures (D. Sette [25]).

the experiment was performed at 25 °C, i.e., at a temperature 4 °C higher than the consolute temperature. The comparison of the results in figures 10 and 11 with those obtained in the liquid-vapor critical region (figs. 3 and 5) shows that in the critical solubility case the processes which give rise to additional losses operate in a wider range of temperature around the critical one. This fact

indicates an essential difference between the two types of systems.

Various attempts have been made to find out what the process responsible for the largest part of losses in these systems is. The dissipative causes which have been examined are viscosity, relaxation, and scattering. Let us briefly review the research made on this subject.

3.1. Viscosity and Thermal Conductivity

Different from the case of liquid-vapor critical media, the viscosity coefficient (η) of mixtures formed by partially soluble liquids undergoes a large increase when temperature approaches the critical one. However, the classical losses due to this fact, i.e., calculated with Stokes' formula for an homogeneous medium, would be still inadequate to explain the experiment: the total viscosity absorption coefficient would amount to a few per mille of the observed value.

The fluid however is not homogeneous. R. Lucas [27] has calculated the sound absorption coefficient when density fluctuations are present in the liquid. Lucas assumes that the density fluctuations are time independent and isotropic and that the sound velocity does not vary along the direction of propagation. Moreover he maintains Stokes' relation between the two viscosity coefficients. The absorption coefficient then results

$$\alpha_{\eta}^* = A\nu^2 + B \quad (3)$$

where

$$A = \frac{8\pi^2}{3} \frac{\eta}{\rho_0 c^3} \left(1 + \frac{1}{\tau} \int_0^{\tau} s^2 d\tau \right)$$

$$B = \frac{10}{9} \frac{\eta}{\rho_0 c} \frac{1}{\tau} \int_0^{\tau} \left(\frac{\partial m}{\partial x} \right)^2 d\tau$$

and ρ_0 the average density; ρ the local density; $m = \frac{\rho_0}{\rho}$; s , the condensation, given by $\rho = \rho_0 (1 + s)$; $d\tau = dx dy dz$ the volume element of the liquid. A and B depend upon the properties of the liquid and the density fluctuations in it, but they are frequency-independent. As a consequence of the presence of density fluctuations, the expression of the absorption coefficient has two corrective terms for Stokes' expression

$$\alpha_{\eta} = \frac{8\pi^2}{3} \frac{\eta}{\rho_0 c^3} \quad (4)$$

The first corrective term has the same frequency dependence of the Stokes' term, the second one is constant with frequency. The parameter $\frac{\alpha_{\eta}^*}{\nu^2}$ therefore decreases with frequency. Such behavior is gen-

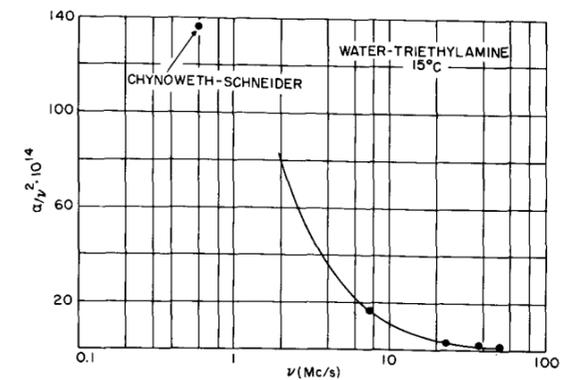


FIGURE 12. α/ν^2 versus frequency for a water-triethylamine mixture at 15 °C (D. Sette [25]).

erally found in these kinds of mixtures; figure 12 [25] gives some results for a mixture water-triethylamine with 44.6 wt percent of amine. Unfortunately, however, a similar decrease of $\frac{\alpha}{\nu^2}$ with frequency can be expected also in the case of other dissipative effects, mainly of the relaxation type.

A calculation using the Lucas' formula has been carried out for the water triethylamine mixture for which data on the thermodynamic behavior of the system are available. Rough approximations were introduced; the results seem to indicate however that, though the viscosity losses in the inhomogeneous medium are higher than those given by Stokes' formula and may become of some importance at low frequencies, they are still insufficient to explain the largest part of the observed attenuation.

Another cause of losses is the existence of thermal conductivity. The corresponding contribution to absorption coefficient in normal liquids is much smaller than the viscosity term. Although thermal conductivity determinations in critical region are missing in the literature, it seems unlikely that thermal conductivity substantially contributes to the large absorption found in the critical media.

3.2. Scattering

A rough description of the medium is obtained by thinking of the system as formed by a mother phase in which clusters of various sizes and compositions are dispersed. The presence of inhomogeneities may lead, as in the case of liquid-

vapor critical systems, to scattering of sound energy. On the importance of this process the opinions do not entirely agree.

The dimensions of individual clusters as determined by light scattering experiments are of the order of wavelength of visible light ($0.5 \cdot 10^{-6}$ m), i.e., much smaller than the sound wavelength ($\sim 10^{-3}$ m at 1 Mc/s) in the frequency range of experiments: if the clusters acted as individual scatters the contribution of scattering to sound energy loss would be very small. It is however necessary to assume, as in the case of liquid-vapor critical systems, that there actually are strong correlations between fluctuations in adjacent volumes. If one considers Liebermann's theory in which an exponential autorrelation is assumed one finds a dependence of α on frequency which is not much different from proportionality to the fourth power of ν , i.e., $\frac{\alpha}{\nu^2}$

should increase with frequency. This is contrary to some experiments where this parameter has been found decreasing within the range examined: figure 12 refers to water-triethylamine mixtures and similar results have been obtained in nitrobenzene-*n*-hexane (5 to 95 Mc/s).

Liebermann's theory therefore does not seem satisfactory for an explanation of the experimental results, and it is at the present difficult to see whether by using an adequate correlation function, it is possible to explain the entire increase of absorption in the critical mixture by means of scattering.

Some experiments however have definitely shown the existence of scattered energy in a critical mixture when sound goes through it. Recently A. E. Brown and E. G. Richardson [26] have shown this effect in aniline-cyclohexane mixtures. These authors have measured the energy received by a probe whose axis forms an angle θ with the sound beam radiated from the source. At 1.5 and 2.5 Mc/s a broadening ($4 \div 5^\circ$ at 2.5 Mc/s) of the beam radiated has been observed when the source is in the critical mixture. At 5 Mc/s, while the intensity falls to zero (first minimum) at an angle θ of 1.5° if the medium does not contain inhomogeneities when the radiation takes place in a critical mixture one obtains patterns of relative intensities at various angles θ as those shown in figure 13. From the position of maxima and minima the authors calculate dimensions of effective scatters, which are of the order of magnitude of 100 to 400μ (compared with $\lambda = 500\mu$). Table III gives the experimental

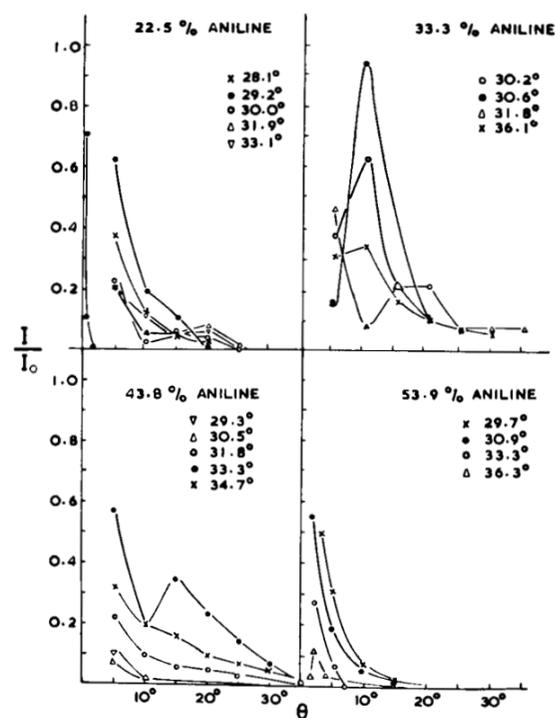


FIGURE 13. Angular distribution of scattered sound at 5 Mc/s in aniline-cyclohexane mixtures (A. E. Brown and E. G. Richardson [26]).

TABLE III

Temperature °C	$f = 1.5$ Mc/s			$f = 2.5$ Mc/s			$f = 5.0$ Mc/s		
	α	α_0	c	α	α_0	c	α	α_0	c
22.5% aniline									
34				0.057	0.011	1262	0.145	0.11	1260
33				0.070	0.030	1262	0.15	0.11	1260
32				0.080	0.035	1262	0.15	0.11	1262
31				0.097	0.023	1262	0.155	0.11	1264
30.5				0.115	0.023	1262	0.17	0.12	1266
30				0.140	0.011	1262	0.185	0.14	1268
29.25				0.105	0.06	1262	0.26	0.145	1270
33.3% aniline									
34	0.042	0.006	1281	0.09	0.055	1282	0.23	0.20	1288
33	0.045	0.007	1284	0.105	0.055	1282	0.23	0.20	1291
32	0.057	0.011	1288	0.130	0.055	1289	0.25	0.17	1288
31	0.060	0.02	1294	0.160	0.055	1289	0.40	0.17	1294
30.5	0.057	0.007	1296	0.132	0.055	1296	0.25	0.20	1297
43.8% aniline									
34	0.050	0.035	1312	0.080	0.063	1318	0.34	0.17	1310
33	0.057	0.035	1317	0.086	0.063	1319	0.27	0.20	1316
32	0.092	0.035	1323	0.130	0.070	1322	0.30	0.15	1322
31	0.083	0.04	1323	0.160	0.046	1319	0.38	0.05	1333
30.5	0.077	0.052	1323	0.140	0.046	1318	0.32	0.03	1342
53.9% aniline									
34	0.040	0.035	1355	0.070	0.052	1360	0.14	0.023	1356
33	0.040	0.035	1355	0.075	0.046	1360	0.16	0.023	1361
32	0.040	0.035	1356	0.087	0.043	1361	0.18	0.023	1360
31	0.055	0.030	1359	0.14	0.058	1371	0.23	0.035	1359
30.5	0.054	0.030	1360	0.115	0.050	1375	0.23	0.029	1365
30	0.080	0.023	1360	0.092	0.058	1379	0.26	0.035	1376

absorption coefficient (α) and the coefficient that Brown and Richardson determine as due to scattering (α_s) for mixtures of the composition examined and at the frequencies used. These results indicate a substantial contribution of scattering to the total losses: in this case, scattering appears to be the most important dissipative process. The authors observe however that, in the limits of experimental error, scattering does not seem satisfactory to explain the totality of losses experimentally found. Using the roughly approximate procedure of subtracting the scattering absorption coefficient from the experimental one, an unexplained part remains which has the same order of magnitude as the absorption coefficient in pure liquids. ($\frac{\alpha}{\nu^2} = 50 \times 10^{-17} \text{ sec}^2 \text{ cm}^{-1}$ in aniline and $200 \cdot 10^{-17}$ in cyclohexane).

3.3. Relaxation Processes

Various researchers have thought that relaxation processes of various kinds may be involved in the propagation of sound waves in critical mixtures and could be responsible for the large absorption experimentally found.

The existence of clusters of various compositions dispersed in a mother phase induces the presence of a great number of equilibria which may be perturbed by the temperature variations due to the sound wave. The kinetics of the system is to be described by reactions which take place either among clusters of different kinds or between clusters and molecules of the mother phase to generate clusters having a new composition. The situation is similar to the one found in binary mixtures of the water-alcohol type when a maximum of the absorption coefficient versus composition is present: in such case, most of the absorption increase seems connected with equilibria which exist among various molecular associations of the two components, and are altered by temperature changes produced by sound waves.

The relaxation processes which arise are of the same kind as those found in liquids where a low rate chemical equilibrium is present and can be described by means of a specific heat function of frequency. Owing to the great number of equilibria present among clusters of various sizes and compositions, a very broad distribution of relaxation times is to be expected. This indication is in agreement with experimental findings: in the case of the

water-triethylamine mixture the experimental results (fig. 12) when interpreted on the basis of the relaxation theory, clearly show this fact; a very rough estimation of the range of relaxation frequencies indicates that it extends at least from 2 to 30 Mc/s.

M. Fixman [28, 29, 30] has recently considered in some detail the manner in which the characteristic fluctuations of critical mixtures may cause a frequency dependence of one or more of the thermodynamical quantities which are of importance in sound propagation; he too has reached the conclusion that the specific heat is the quantity most likely to be involved in the observed behavior. In an early attempt [28], he considered a fluctuating heat capacity associated with density fluctuations; adjacent volumes of the liquid reach different temperatures when passed through by a sound wave: sound energy absorption would appear as a consequence of the heat flow in the equalization of temperature gradients. Such a process however can produce a much smaller absorption than observed experimentally and therefore can not be responsible for the high losses observed. The dissipative effect just mentioned is described in the nonlinear equation of motion and energy transport by a term linear both in the temperature variation produced by the sound wave and in the density or composition fluctuations; in Fixman's early treatment other terms which are either quadratic or of higher order in local fluctuations, were neglected.

In a later study Fixman has found the way to handle the quadratic terms and he was able to show that they are strongly coupled with local temperatures; these terms originate an anomalous static heat capacity in agreement with experiment [31] and a frequency dependent heat capacity which could be responsible for the sound absorption increase in the critical region. In this calculation, the composition is expressed as a function of position by means of a Fourier series or integral, with suppression of all Fourier components having a wave number (k) greater than some k_{max} . It is then possible to obtain a fluctuating entropy density ($\langle \delta s \rangle$) associated with critical composition fluctuations which is perturbed by the temperature variation produced by sound and gives rise to an excess heat capacity per unit volume

$$\Delta = T_c \frac{\langle \delta s \rangle}{\delta T} \quad (5)$$

In the expression of $\langle \delta s \rangle$ enters the radial distribution function $g(r)$ at time t expressed by means of the Fourier components up to k_{\max} . The dynamics of the long range part of $g(r)$ is assumed to satisfy the diffusion equation

$$\frac{dg}{dt} = h[\kappa^2 \nabla^2 g - \nabla^2 \nabla^2 g] \quad (6)$$

being h a diffusion constant which may be related to more usual parameters and κ the reciprocal of an "indirect" correlation length. For a mixture at the critical composition κ can be expressed by means of a short-range correlation length l

$$\kappa^2 = 6 \frac{T - T_c}{l^2 T_c} \quad (7)$$

Fixman's analysis led him to conclude that κ^2 is strongly coupled with local temperature and that this circumstance can be the reason for both the increase of static heat capacity and the appearance of a frequency dependence of specific heat. Therefore he substitutes κ^2 with

$$\kappa^2 + \left(\frac{\partial \kappa^2}{\partial T} \right) \delta T \quad (8)$$

and supposes δT to be sinusoidal function of time. Fixman obtains for the complex dynamic heat capacity per unit volume an expression and furnishes a numerical integration of the real and imaginary part close to the critical point.⁶

This expression can be used to calculate the complex speed of sound from which velocity and absorption are derived. The comparison of these theoretical values with experiment requires the knowledge of: (1) the correlation distance l ; (2) a friction constant, β , which enters in the expression of the diffusion constant; (3) the specific heat per mole in the absence of fluctuation C_p^0 ; (4) the ratio of specific heat $\gamma_0 = \frac{C_p^0}{C_v^0}$ in the same conditions.

The results of the comparison between theory and experiment in the case of the mixture *n*-hexane-aniline (47.6 wt % of hexane) studied by Chynoweth and Schneider are indicated in figure 14. C_p^0 and γ_0 were approximately evaluated by the Author while $\beta = 9.10^{13} \text{ sec}^{-1}$ and $l = 4 \text{ \AA}$ were assumed as reasonable values. It appears that the numerical values of the observed absorption as well as its

⁶The function has been tabulated by Kendig, Bigelow, Edmunds, and Pings [32].

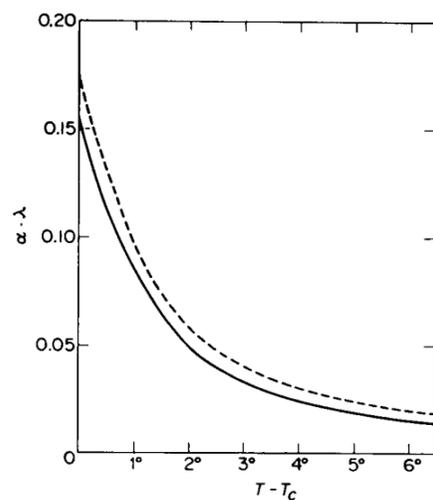


FIGURE 14. Absorption per wavelength versus $(T - T_c)$ for aniline-*n* hexane critical. Solid line theoretical, dashed line experimental. (M. Fixman [29]).

variation with temperature could be explained by Fixman's theory. The theory should be tested for the variation of absorption coefficient with frequency.

Fixman's calculation predicts a very small velocity dispersion and this result could be in agreement with experiment because no dispersion has been so far detected in the limits of errors. The variation of velocity with temperature indicated by the theory (3% for a temperature increase of 5 °C above the critical point) is about twice the change observed. Fixman's theory, which could be extended to a liquid-vapor critical system supports the idea that relaxation processes may be an important, if not the most important, dissipation process in the critical systems.

4. Conclusions

At the present status of research, most of the high absorption found in liquid-vapor and liquid-liquid critical systems is most likely due to one or both of the two processes: (1) scattering by inhomogeneities due to density or composition fluctuations, (2) relaxation in the cluster equilibria perturbed by the temperature variations induced by sound waves. It is not possible, at present, to go much further in specifying what the most important process may be in particular cases.

It is to be mentioned at this point that recently A. S. Sliwinski and A. E. Brown [33] have stressed the importance of a strong difference existing between critical mixtures and liquid-vapor critical systems. In the first case, in fact, the equalization of composition fluctuations must proceed through a diffusion mechanism which is particularly slow near the critical point; instead, the merging of two or more density fluctuations to form a uniform region in a liquid-vapor critical medium does not require diffusion. Such a difference could play an important role when the sound wavelength is either smaller or of the same magnitude than the linear dimension of assemblies: this is the normal case when ultrasonic waves interact with critical systems. The sound wave produces a variation of the pressure and temperature of assemblies around values which are near the critical ones: in the case of liquid-liquid system, as a consequence of the slowness of diffusion in the short time in which the interface between assemblies disappears, the passage of sound does not strongly affect the form and size of assemblies; in the case of liquid-vapor the assemblies lose their identity when the surface tension disappears and they may reappear successively in a form quite different from the original

configurations.⁷ To support this point of view, Sliwinski and Brown have considered some other experiments which indicate the different ways of interaction of sound waves with a liquid-liquid critical mixture and a liquid-vapor critical system. The striations which can be observed with a Schlieren setup in a medium at rest are not significantly changed when sound is applied in the liquid-liquid case, while they are broken in liquid-vapor systems as though a pulverization of assemblies had taken place. A similar effect is evident when one follows the light diffraction patterns produced by a sound wave in the medium with time after sound application. In figure 15 the light diffraction pattern in an aniline-cyclohexane mixture at 31 °C, in carbon dioxide at 3.5 °C and 72 atm, and in ethylene at 9.6 °C and 52 atm are shown at $\frac{1}{12}$ sec intervals from the instant when sound (1 Mc/s) is switched on (arrow). While the patterns remain unchanged in the liquid-liquid critical mixture; they rapidly become blurred in the liquid-vapor case.

⁷The existence of substantial differences between assemblies in the two types of critical systems is also shown by the temperature dependences of α experimentally found (figs. 3, 5, and 10).

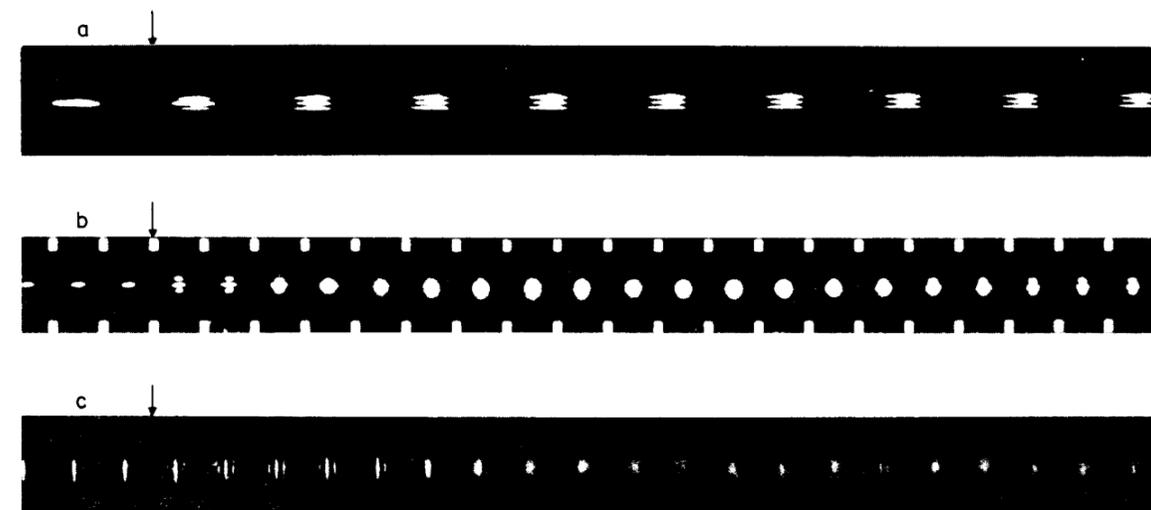


FIGURE 15. Light diffraction pattern produced by sound (1 Mc/s) in aniline-cyclohexane mixture at 31 °C (a) in CO₂ at 3.5 °C and 72 atm (b), in ethylene at 9.6 °C and 52 atm (c) the photographs were taken at $\frac{1}{12}$ sec intervals. Arrows show turning on of the sound. (A. S. Sliwinski and A. E. Brown [33]).

It would seem therefore that sound has a tremendous effect on the structure of assemblies in the liquid vapor case while it does not practically affect the configuration of clusters in critical mixtures. Sliwinski and Brown think that this could be an indication of the fact that scattering is particularly important in critical mixtures while it must be less significant in liquid vapor media: in the last case structural relaxation effects would be the main cause of absorption.

The survey of the work so far carried out in critical systems has shown how the problems associated with the propagation of sound waves in critical media have not yet been solved. At present, they seem to be posed in clearer terms than some years ago, but much theoretical and experimental research is needed. The important areas of research are essentially two: (a) the low-frequency sound velocity at the critical point; (b) the analysis of absorption and possibly, of dispersion of sound waves. The progress of experimental techniques should today allow more precise determinations of sound velocity and of the absorption coefficient; moreover, it is important to extend the ranges of temperature, frequency and composition in which the measurements are made. From the theoretical side, we expect progress in the thermodynamical treatment of critical systems, in scattering theories adequately considering correlation between fluctuation in adjacent volumes, in separating the contributions to absorption due to relaxation and scattering processes when they are of comparable importance.

The profit of these researches will surely be rewarding in establishing the characteristics and the behavior of critical systems since sound propagation is so intimately connected with the particular nature of these media.

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Ultrasonic Investigation of Helium Near its Critical Point

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The recent discovery of a logarithmic singularity in the specific heat at constant volume C_V of fluids at the critical point [1-3] has stimulated renewed interest in this region. A consequence of this singularity that was soon demonstrated [4, 5] is that the adiabatic compressibility κ_s must likewise be singular and the velocity of sound, given by $u^2 = 1/\rho\kappa_s$, must go to zero. We have accordingly measured the sound velocity in He^4 at a frequency of 1 Mc/s in the critical region. Some of the results of these measurements are reported herein.

Figure 1 shows the velocity as a function of temperature along an isobar and as a function of pressure along an isotherm passing approximately through the critical point. These measurements have been reported previously [5, 6] (together with a description of the experimental techniques, which will not be repeated here). However, we have subsequently found that, as a result of slight hysteresis and lack of reproducibility in the pressure gauge used in the experiment, the pressure and temperature of this isobar and isotherm should probably be increased by about 4 mm Hg and 0.003 °K, respectively. We are currently making measurements along families of closely spaced isotherms passing through the critical region, and find that the shape of an isotherm is substantially independent of its temperature over a range of several millidegrees. We therefore believe that our conclusions will not be seriously affected by the above-mentioned correction, but final judgement must be reserved until our measurements are complete.

It can be seen from figure 1 that the general behavior is in agreement with expectation; the velocity falls rapidly as the critical point is ap-

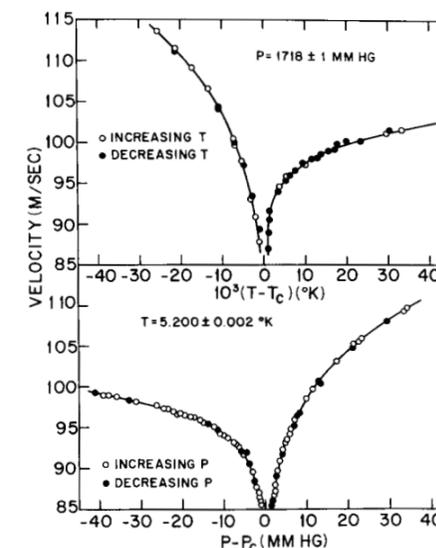


FIGURE 1. Sound velocity as a function of temperature (a) and pressure (b) in the critical region.

proached from any direction, and it is not unreasonable to suppose that it goes to zero at the critical point itself. Unfortunately, the large attenuation in this region makes it impossible to approach the critical point more closely with the present apparatus. We can thus only draw inferences about the behavior closer to the critical point by interpretation of the data we have; this is the subject of the following paragraphs.

We note first that a plot of $1/u^2$ as a function of $\log |T - T_c|$ or $\log |P - P_c|$ is very nearly linear over the range of our data; there thus appears to be a logarithmic singularity in this quantity at the critical point. This fact is of interest as an experimental result independent of any theory. However,

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