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Pressure effects and ultrasonic attenuation in the binary liquid mixture 3-methylpentane and nitroethane near the critical point

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Experiments are reported in which a critical mixture of 3-methylpentane plus nitroethane has been subjected to varying pressures. By varying the static pressure we have determined the dependence of the critical temperature on pressure with considerable accuracy. By sudden depressurization we have cooled the sample adiabatically leading to phase separation via spinodal decomposition; from these experiments we have determined the adiabatic thermal pressure coefficient near the critical point. By combining our data with the experimental density data of Greer and Hocken, we are able to determine the asymptotic critical behavior of the thermal-expansion coefficient and of the specific heat, consistent with two-scale-factor universality. We also obtain a value for the adiabatic coupling constant which appears in the dynamic scaling theory for the frequency dependence of the critical sound attenuation. Our thermodynamic data appear to be in good agreement with the critical ultrasonic attenuation data obtained by Ishida and Harada for 3-methylpentane plus nitroethane.

I. INTRODUCTION

The principle of critical-point universality asserts that one-component fluids near the gas-liquid critical point and binary liquids near the critical mixing point belong to the same universality class. Because of the absence of strains in fluids it is possible to approach the critical point very closely. Such experiments have confirmed the validity of the principle of critical-point universality for fluid systems in considerable detail.[1-3]

Strictly speaking, a binary liquid near the critical mixing point is analogous to a one-component fluid near the gas-liquid critical point only if in the former system P or P/T is kept constant, where P is the pressure and T the temperature.[4,5] Binary liquids near the critical mixing point have an extra degree of freedom which is readily accessible experimentally by varying the pressure. In this respect, phase separation in binary liquid mixtures has many similarities with the superfluid phase transition at the λ line in liquid helium.[6,7]

These considerations motivated us to make a study of the pressure dependence of critical phase separation in a binary liquid mixture. Previous work in our laboratory yielded an accurate determination of the static and dynamic behavior of the critical fluctuations in the binary liquid 3-methylpentane plus nitroethane.[8,9] For the present study we therefore continued to use this binary liquid system.

It is possible to consider two kinds of pressure-dependent effects. First, one can study the critical-point phase transition parameters as a function of the static pressure P. Second, by suddenly changing the pressure one can quench the system from a stable state in the one-phase region to an unstable state in the two-phase region, thus inducing phase separation via spinodal decomposition. We have performed both kinds of experiments.

First, by changing the static pressure we have determined the critical temperature T_c as a function of the pressure P, thus locating the critical line in the P-T diagram. These results supplement and improve upon similar information previously reported by Beysens and Tufeu for the same system.[10]

Second, we have induced spinodal decomposition by cooling the system adiabatically as a result of a fast change of the pressure. Spinodal decomposition experiments in binary liquid mixtures have been reported by several investigators.[11-18] In these experiments spinodal decomposition was induced either by changing the temperature[11-14,18] or by changing the pressure of the system.[15-18] Inducing spinodal decomposition by a fast pressure quench has two advantages over the alternative method in which spinodal decomposition is induced by adding (or subtracting) heat to the fluid. First the speed with which the pressure can be changed makes it possible to observe earlier stages of spinodal decomposition. Furthermore, the adiabatic cooling as a result of the pressure change occurs homogeneously throughout the entire fluid sample. Although the experimental procedure is similar to that used by Knobler and coworkers,[15–17] the physical basis of our method of inducing spinodal decomposition is somewhat different. In the experiments of Knobler and coworkers[15–17] and of Wenzel *et al.*[18] spinodal decomposition was induced by changing the critical temperature of the system as a result of a pressure jump. In our method, spinodal decomposition is induced by lowering the temperature of the system itself through adiabatic cooling with a fast pressure quench. It is not the purpose of this paper to report a detailed study of the spinodal decomposition process itself. Rather, the occurrence of spinodal decomposition is used as an indication that the system has passed through the phase transition. As will be discussed in further detail, the phenomenon of spinodal decomposition is used as a tool to locate the adiabatic cooling line in the *P*-*T* diagram for the system at its critical composition. From the slope of the adiabat and the slope of the critical line we then determine an adiabatic coupling constant which appears in the dynamic scaling theory of critical ultrasonic attenuation.[19,20]

II. EXPERIMENTS

A. Apparatus

The binary liquid to be studied was contained in a cylindrical optical cell located at the end of a U tube which contained a mercury column as a pressure separator. The arrangement is shown schematically in Fig. 1. The cylindrical sample cell, with an optical path length of 10 mm and a volume of 3 cm^3, was a Markson optical cell modified for our experiments. The fritted flat windows were more firmly attached to the cell body by heating the edges lightly with a torch, leaving the center area undistorted. To further guard against failure under sudden pressure changes, the flat windows were reinforced with two stainless steel disks, machined to accommodate a rubber O ring whose diameter was equal to the diameter of the cell. Used in conjunction with spacers as indicated in Fig. 1(b), the O ring and disk assembly reinforced the cell windows so that they could readily withstand the pressure changes of up to 5 atmospheres used in the experiments. The liquid samples could be stirred with the aid of a glass-encapsulated magnetic stir bar also located in the sample cell. The optical sample cell was joined to a U-shaped pyrex tube with an internal diameter of 5 mm [Fig. 1(a)]. The interior of the U tube below the sample cell was roughened by grinding. The arrangement of sample cell with U tube is similar to the arrangement used by Wong and Knobler for observing spinodal decomposition in isobutyric acid plus water mixtures.[15] However, since the turbidity of 3-methylpentane plus nitroethane is much smaller than that of isobutyric acid plus water, no special precautions were needed to reduce the optical cell path length for our experiments. A general problem encountered in experiments with binary liquids under varying pressures is the fact that the critical temperature T_c easily drifts with the time owing to leakage of impurities into the liquid sample.[15] These problems were also encountered in our preliminary experiments. However, it was found that the drift problem could be relieved by using glass-covered stir bars in the liquid and by roughening part of the interior of the U tube, thus slowing the diffusion of impurities along the inner wall of the U tube.

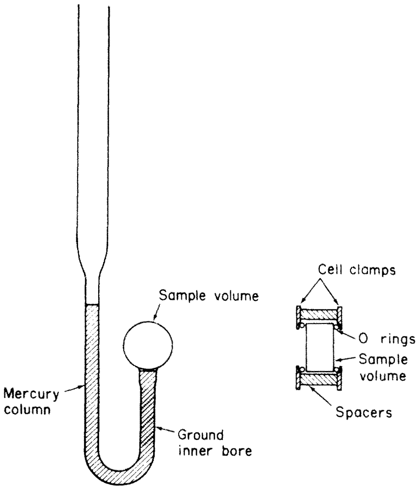

FIG. 1. Glass sample cell and U tube.

The sample cell and U tube were located in a glass-walled thermostat containing about 20 gallons of water. The bath temperature was controlled to within ±0.15 mK over a period of about an hour and to within ±0.3 mK over a period of 24 h with the aid of a Tronac PTC 40 controller. The temperature was measured with a Hewlett-Packard quartz thermometer. The frequency of oscillation is about 28 MHz with a temperature coefficient of 0.9865 kHz/°C. We monitored this frequency with a resolution of 0.1 Hz using an electronic counter and a rubidium frequency standard with a stability of 1×10^{-10} per month. The calibration supplied with the crystal was verified by a comparison against a secondary thermistor standard made available to us by S. C. Greer.

The arrangement for changing the pressure of the binary liquid mixture is shown in Fig. 2. The pressure delivery system, using nitrogen as pressurizing agent, was connected to the exit end of the U tube

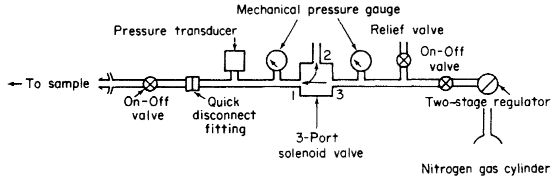

FIG. 2. Schematic representation of pressure delivery system.

attached to the sample cell. A solenoid valve controls the supply of nitrogen pressure from a nitrogen gas cylinder. With the aid of an on-off valve and a quick-connect fitting, located close to the U tube, the binary liquid could be pressurized, sealed off, and disconnected. The pressure was registered with a Setra model 204 pressure transducer with a pressure range of 250 psi and a response of 0.02004 V/psi.

To prepare the liquid samples, use was made of commercially available 3-methylpentane with a purity better than 99.9% and nitroethane with a purity of 97%. The nitroethane was dried over gas chromatography-grade silica gel to remove any possible traces of water. No further purification was attempted, since the purpose of the experiment was not to measure T_c of the mixture on an absolute basis, but rather the change in T_c as a function of pressure. The experiments to be reported were performed with two different samples. Both samples were made by injecting the liquid components into the cell through the mercury column with the aid of a syringe, a hypodermic needle, and a long teflon tube. In preparing the first sample, the mass transfer was monitored on a sensitive balance. In preparing the second sample, micrometer syringes were used to accurately deliver known volumes of the two liquids. Care was taken to avoid air bubbles. All handling was done in a dry nitrogen glove box. The two samples, A and B, prepared for the experiments had a concentration $x_{\mathrm{NE}}=0.505\pm0.007$ and $x_{\mathrm{NE}}=0.499\pm0.007$, respectively, where x_{NE} indicates mole fraction of nitroethane. These concentrations are close to the critical concentration estimated as $x_{\mathrm{NE}}=0.500$.[21] The experiments confirmed that the meniscus would form near the middle of the sample cells. The critical temperature of 3-methylpentane plus nitroethane is approximately 299.60 K. The critical temperature T_c of sample A was found to have changed by only 7 mK after nine months, corresponding to a drift of 0.8 mK/month. The measurements with sample B lasted only about one week; during this time interval a drift of 0.5 mK of T_c was noted, only slightly larger than the experimental critical temperature uncertainty of ±0.2 mK.

B. Pressure dependence of the critical temperature

The critical temperature $T_c(P)$ as a function of pressure was determined by visual observation. It turns out that the derivative dT_c/dP is rather small for 3-methylpentane plus nitroethane and considerable accuracy in determining T_c was needed so as to obtain a reliable value. We performed a number of preliminary experiments during which the binary liquid sample was cooled slowly toward T_c in steps of approximately 0.3 mK, with about 20 minutes of waiting time between temperature settings. It was established that the early appearance of vertical striations due to fluid flow would inevitably indicate that the separation temperature had been reached. This phenomenon enabled us to determine the separation temperature with an accuracy of about 0.2 mK within five or ten minutes after the appropriate temperature had been reached, thus avoiding the problem of long waiting times of the order of hours. Care was taken that the same procedure was used for measuring T_c at each pressure to eliminate the effects of any systematic errors as a result of the chosen measurement procedure. Furthermore, before each measurement of $T_c(P)$ at a given pressure P, we redetermined the critical temperature $T_c(P_0)$ corresponding to the atmospheric pressure P_0 so as to eliminate any possible drifts of T_c with time.

We performed three experimental runs: run 1 and run 2 with the same sample A but separated by a

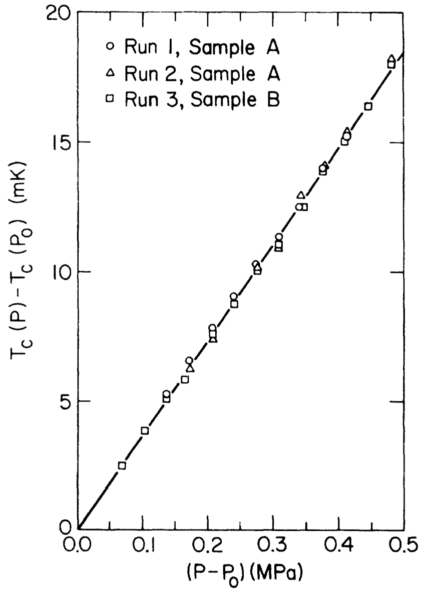

FIG. 3. Enhancement of the critical temperature $T_c(P)$ over the critical temperature $T_c(P_0)$ at atmospheric pressure for 3-methylpentane plus nitroethane.

time interval of six months, and run 3 with a different sample *B*. The experimental data obtained for the increase of the critical temperature $T_c(P)$ over the critical temperature $T_c(P_0)$ at atmospheric pressure P_0 are presented in Table I and plotted in Fig. 3 as a function of the pressure difference $P-P_0$. The data cover a range of about 0.5 MPa (=5 bar). In the interpretation of the data we assume that the change of the critical concentration x_c with pressure is negligibly small so that the separation temperature at elevated pressures can still be identified with the critical temperature of the mixture. Arguments in support of this assumption have been presented by Wong and Knobler.[15] In our case the assumption was confirmed by the observation that at elevated pressures the meniscus would continue to appear at the same position in the sample cell.

As can be seen from Fig. 3 the critical temperature T_c varies linearly with pressure to well within the experimental accuracy. A fit of the data to a straight line yields the result

$$\begin{aligned} T_c' \equiv dP/dT_c &= (3.67\pm0.06)\times10^{-8}\ \text{K/Pa} \\ &= (3.67\pm0.06)\ \text{mK/bar}\ , \end{aligned} \tag{2.1}$$

where the quoted error represents *two* standard deviations. This value of T_c' is smaller than that observed for many binary liquids.[22] In particular, it is a factor of 10 smaller than the value earlier estimated by Klein and Woermann for 3-methylpentane plus nitroethane.[23] We also note that the coefficient T_c' of 3-methylpentane plus nitroethane is positive as it is for many other liquid mixtures, but this is in contrast to the coefficient T_c' of the isobutyric acid plus water system, which is negative.[24,25]

The variation of T_c with pressure for 3-methylpentane plus nitroethane was also investigated by Beysen and Tufeu.[10] While our data were taken at pressures up to 5 bar over atmospheric pressure, Beysens and Tufeu measured T_c at pressures from 5 to 130 bar and concluded $T_c' = (3.7\pm0.5)\times10^{-8}$ K/Pa. This result is in excellent agreement with the more accurate value deduced above from our experimental data. The data reported by Beysens and Tufeu are reproduced in Fig. 4. The line in this figure was not obtained from a fit to these data, but represents the linear behavior extrapolated from our data. The good agreement indicates that the variation of T_c with P is linear over a large pressure range.

In an earlier study of the effect of pressure on liquid immiscibility, Meyers *et al.*[20] considered an approximate relationship between dT_c/dP and the molar excess volume V^E and molar excess enthalpy H^E of the form

$$T_c' \simeq T_c \frac{V^E(T_c,x_c)}{H^E(T_c,x_c)}\ , \tag{2.2}$$

where the ratio V^E/H^E is to be evaluated at the critical point. Data for the excess volume and enthalpy of 3-methylpentane plus nitroethane have been reported by Knobler and co-workers.[26,27] From these data we estimate $V^E(T_c,x_c) = (0.218\pm0.004)$ cm^3/mol and $H^E(T_c,x_c) = (1626\pm100)$ J/mol. We thus obtain $T_c V^E(T_c,x_c)/H^E(T_c,x_c) = (4.0\pm0.3)\times10^{-8}$ K/Pa which indeed reproduces our observed value of $T_c' = (3.67\pm0.06)\times10^{-8}$ K/Pa within 10%. We conclude that the experimental data for

TABLE I. Critical temperature as a function of pressure.

Run 1, sample *A*		Run 2, sample *A*		Run 3, sample *B*	
$P-P_0$ (MPa)	$T_c(P)-T_c(P_0)$ (mK)	$P-P_0$ (MPa)	$T_c(P)-T_c(P_0)$ (mK)	$P-P_0$ (MPa)	$T_c(P)-T_c(P_0)$ (mK)
0.1372	4.9±0.4	0.1729	5.8±0.2	0.0687	1.7±0.2
0.1715	6.0±0.2	0.2071	7.0±0.4	0.1032	3.0±0.2
0.1717	6.4±0.2	0.2752	9.7±0.3	0.1360	4.3±0.2
0.2060	7.4±0.2	0.3103	10.5±0.3	0.1649	5.0±0.2
0.2063	7.5±0.3	0.3436	12.5±0.3	0.2066	6.8±0.2
0.2397	8.6±0.4	0.3785	13.6±0.3	0.2400	7.9±0.3
0.2749	9.9±0.2	0.4130	14.9±0.4	0.2415	8.0±0.2
0.3101	11.0±0.2	0.4814	17.7±0.4	0.2751	9.0±0.3
0.3406	12.1±0.3			0.2761	9.4±0.2
0.3767	13.6±0.2			0.3092	10.2±0.3
0.4130	14.8±0.3			0.3445	11.7±0.2
0.4131	14.8±0.2			0.3772	13.1±0.2
				0.4120	14.2±0.1
				0.4462	15.5±0.2
				0.4826	17.0±0.2

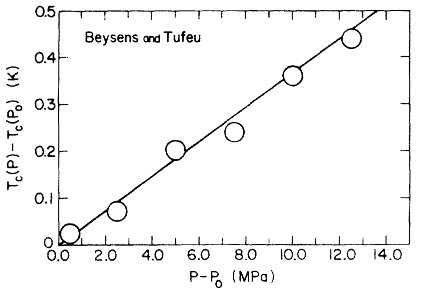

FIG. 4. Enhancement of the critical temperature $T_c(P)$ over the critical temperature $T_c(P_0)$ at atmospheric pressure for 3-methylpentane plus nitroethane as determined by Beysens and Tufeu.[10] Solid line represents the linear behavior extrapolated from our experimental data.

3-methylpentane plus nitroethane are consistent with the approximate relationship (2.2).

C. Adiabatic cooling and spinodal decomposition

A binary liquid near its critical point can be brought from the stable one-phase region into the unstable spinodal region by a pressure quench. Our experimental setup allowed us to change the pressure of the binary liquid in less than 15 msec. Periodic pressure changes can also be investigated with this apparatus; such a procedure could be used to stabilize the process of spinodal decomposition in analogy with similar stabilization methods encountered in plasma physics, electronics, and mechanics.[28] The interest of such experiments was also recently pointed out by Onuki.[29]

The effect of a pressure quench is twofold: it changes the critical temperature because of the pressure dependence of T_c and it changes the temperature of the system as a result of the adiabatic expansion or compression. The rate of change of the temperature of the system is determined by the magnitude of the adiabatic thermal pressure coefficient $(\partial P/\partial T)_{S,x_c}$. Hence, what actually happens upon a fast pressure quench of a system near the critical temperature depends on the magnitude of the slope $T_c' = dT_c/dP$ of the critical line as compared to the inverse adiabatic thermal pressure coefficient $(\partial T/\partial P)_{S,x_c}$. In many binary liquids

$$\left|\frac{dT_c}{dP}\right| > \left|\left(\frac{\partial T}{\partial P}\right)_{S,x_c}\right|$$

at the temperatures of interest. Previous investigators have thus induced spinodal decomposition in binary liquids by changing T_c with a pressure jump.[11-18] However, for 3-methylpentane plus nitroethane

$$\frac{dT_c}{dP} < \left(\frac{\partial T}{\partial P}\right)_{S,x_c} .$$

Therefore, for this system, although $T_c' > 0$, spinodal decomposition is induced by cooling the system adiabatically as a result of depressurizing the system. We have used this effect to make a quantitative study of the adiabatic thermal pressure coefficient of 3-methylpentane plus nitroethane near the critical point.

In our experiments we pressurized the binary liquid sample and, by subsequently heating and mixing the liquid mixture, ensured that it was in the stable one-phase region. Having maintained the system at a given pressure P and a given temperature T above the known critical temperature $T_c(P)$, we then suddenly depressurized the sample to atmospheric pressure P_0. At the same time we observed on a screen the light from a 5-mW He-Ne laser beam that was scattered upon traversing the sample, as indicated schematically in Fig. 5. When the system entered the unstable region below the critical temperature, a ring of scattered light appeared on the screen at an angle of about 4°, indicating spinodal decomposition. This visible ring appeared within 5 to 10 sec after the initiation of an appropriate pressure decrease, which we henceforth call a "quench." In spite of this time delay, we take the observation of the ring as evidence that the spinodal decomposition process was set into motion at the time of the quench.

For every given temperature difference $\Delta T = T - T_c(P_0)$ we determined two closely spaced pressure quenches $\Delta P = P - P_0$, the larger leading to the appearance of a spinodal decomposition ring; with the smaller quench, spinodal decomposition did not occur. It was found that this criterion determined the magnitude of the pressure quench $\Delta P = P - P_0$ quite sharply. We therefore adopt the appearance of spinodal decomposition as an internal thermometer indicating that the system has reached a certain temperature T_s which, as we shall see, is just below the critical temperature $T_c(P_0)$.

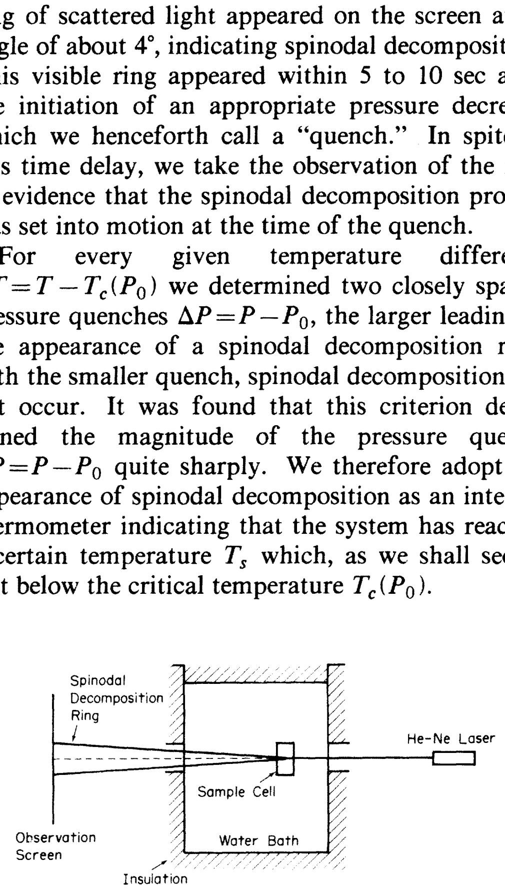

FIG. 5. Schematic representation of experimental arrangement for observing spinodal decomposition.

TABLE II.
Temperature difference $\Delta T = T - T_c(P_0)$ as a function of the adiabatic pressure change $\Delta P = P - P_0$.

Run 1, sample A		Run 2, sample B		Run 3, sample A		Run 4, sample A[a]	
ΔP (MPa)	ΔT (mK)	ΔP (MPa)	ΔT (mK)	ΔP (MPa)	ΔT (mK)	ΔP (MPa)	ΔT (mK)
0.1080	20.7±0.3	0.1207	22.8±0.3	0.1986	39.0±0.5	0.2063	39.6±0.5
0.1564	30.6±0.3	0.1545	29.8±0.3	0.2605	51.5±0.3	0.2679	51.6±0.4
0.1568	30.9±0.2	0.1926	37.6±0.3	0.3001	60.6±0.3	0.2996	60.5±0.3
0.1914	38.2±0.2	0.2070	41.6±0.3	0.3391	68.6±0.2	0.3470	68.6±0.5
0.2338	46.6±0.3	0.2481	49.9±0.2				
0.2654	53.4±0.2	0.2898	58.0±0.4				
0.2913	59.1±0.2	0.3077	61.8±0.2				
0.3191	65.0±0.2	0.3380	68.0±0.2				
		0.3408	68.0±0.3				

[a] Sample A placed in air jacket as discussed in text.

We performed two extensive experimental runs: run 1 with sample A and run 2 with sample B. The values observed for $\Delta P = P - P_0$ as a function of the temperature difference $\Delta T = T - T_c(P_0)$ are presented in Table II and plotted in Fig. 6. Our data cover the temperature range

$$0.02\ \mathrm{K} \leq \Delta T \leq 0.07\ \mathrm{K}\ . \tag{2.3}$$

As can be seen from Fig. 6 the temperature depends linearly on the pressure in this temperature range. From the data we deduce for the slope at $\Delta T \simeq 45$ mK

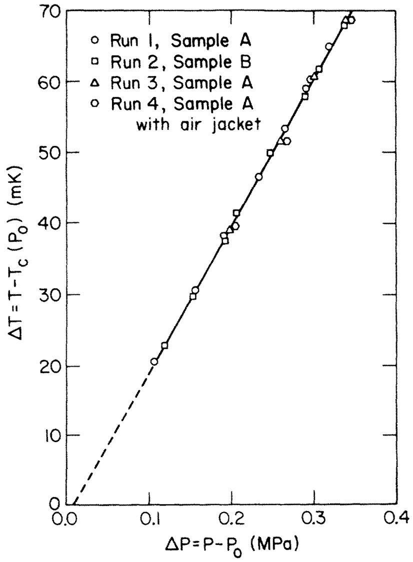

FIG. 6. Minimum pressure quench $\Delta P = P - P_0$ as a function of $\Delta T = T - T_c(P_0)$ needed to induce spinodal decomposition starting from the one-phase region at pressure P and temperature T.

$$\left[\frac{\partial T}{\partial P}\right]_{S,x_c} = (20.8 \pm 0.4) \times 10^{-8}\ \mathrm{K/Pa}$$

$$= (20.8 \pm 0.4)\ \mathrm{mK/bar}\ , \tag{2.4}$$

where the quoted error represents *two* standard deviations.

To identify our experimentally observed thermal pressure coefficient with the adiabatic coefficient we need to assume that any temperature rise of the liquid sample due to heat exchange with the surroundings is negligibly small during the time scale of our experiment. As a precaution we performed two additional runs with sample A, a run 3 with the same conditions as before and a run 4 during which the sample cell was surrounded by an air jacket, thus drastically reducing the heat exchange with the surrounding thermostat. The results of these runs are also included in Fig. 6. Run 3 without the air jacket yielded

$$\left[\frac{\partial T}{\partial P}\right]_{S,x_c} = (21.3 \pm 0.9) \times 10^{-8}\ \mathrm{K/Pa}$$

and run 4 with air jacket yielded

$$\left[\frac{\partial T}{\partial P}\right]_{S,x_c} = (21.4 \pm 1.5) \times 10^{-8}\ \mathrm{K/Pa}\ .$$

We conclude that heat exchange effects during the fast pressure quench are indeed negligibly small. Further details concerning these experiments are contained in a separate report.[30]

When the observed adiabat, as shown in Fig. 6, is extrapolated linearly to zero pressure quench, $\Delta P = 0$, it does not pass through the origin, but appears to intersect the temperature axis at

$\Delta T = -(1.9 \pm 0.4)$ mK. If we were to assume that the slope of the adiabat is a constant independent of temperature, this result would mean that the temperature T_s at which spinodal decomposition is observed is such that T_c-T_s is about 1.9 mK. However, as we shall discuss below, the assumption that $(\partial T/\partial P)_{S,x_c}$ remains constant is incorrect. In fact, $(\partial T/\partial P)_{S,x_c}$ decreases closer to T_c and approaches a limiting value equal to $T_c' = dT_c/dP$; this behavior causes the adiabat to intersect the negative temperature axis closer to the origin than that expected on the basis of a linear extrapolation.

III. SLOPE OF ADIABAT AND ADIABATIC COUPLING CONSTANT g

A. Slope of the adiabat

Our experiments have yielded the critical line and an adiabat in the P-T diagram of 3-methylpentane plus nitroethane at the critical composition. The location of these lines in the range covered by our measurements is shown in Fig. 7. For a thermodynamic description of the system it is convenient to change the variables P and T to the variables P and ΔT, such that

$$\Delta T = T - T_c(P) \,. \tag{3.1}$$

The advantage of these variables is that partial differentiation with respect to P at constant ΔT yields derivatives that do not have a singular critical behavior. Along the adiabat we have

$$\delta S = \left[\frac{\partial S}{\partial P}\right]_{\Delta T} \delta P + \left[\frac{\partial S}{\partial \Delta T}\right]_P \delta \Delta T = 0 \,,$$

so that

$$\left[\frac{\partial T}{\partial P}\right]_S = T_c' + \left[\frac{\partial \Delta T}{\partial P}\right]_S = T_c' - \frac{T}{C_P}\left[\frac{\partial S}{\partial P}\right]_{\Delta T} \,, \tag{3.2}$$

where C_P is the isobaric heat capacity. From now on we adopt the convention that all thermodynamic derivatives are taken at constant $x = x_c$ without denoting this constraint explicitly. Furthermore, in this paper all extensive thermodynamic properties, such as the specific heat C_P and the entropy S, are taken per unit mass. At the critical point $(\partial S/\partial P)_{\Delta T}$ approaches the finite value

$$\lim_{\Delta T \to 0} \left[\frac{\partial S}{\partial P}\right]_{\Delta T} = \frac{dS_c}{dP} \equiv S_c' \,. \tag{3.3}$$

Since the specific heat diverges at the critical point, it thus follows that the slope of the adiabat should approach the slope of the critical line[31,32]

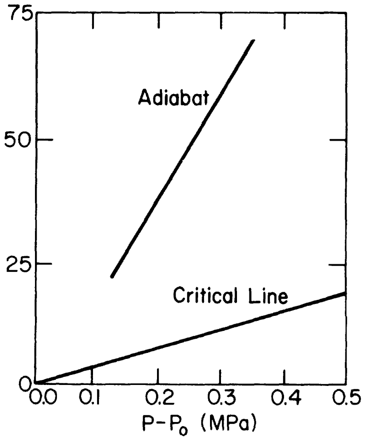

FIG. 7. Critical line and an adiabatic cooling line in the P-T diagram for 3-methylpentane plus nitroethane at the critical composition as deduced from our experiments. Origin corresponds to the critical state at atmospheric pressure $P - P_0$.

$$\lim_{\Delta T \to 0} \left[\frac{\partial T}{\partial P}\right]_S = T_c' \,. \tag{3.4}$$

That is, the adiabat should pass through the critical line in a direction tangential to the critical line. However, from (2.1) and (2.4), as well as from Fig. 7, we see that the value measured for $(\partial T/\partial P)_S$ at $\Delta T \simeq 45$ mK is in fact very different from the slope T_c'.

To reconcile these observations we note that the slope of the adiabat satisfies the thermodynamic relation[6,7,31]

$$\left[\frac{\partial T}{\partial P}\right]_S = \frac{T\alpha_P}{\rho C_P} \,, \tag{3.5}$$

where ρ is the mass density and $\alpha_P \equiv \rho(\partial \rho^{-1}/\partial T)_P$ the thermal expansion coefficient. The asymptotic behavior of α_P and C_P can be represented by power laws of the form

$$\alpha_P = A_0 \epsilon^{-\alpha} + A_1 \,, \tag{3.6}$$

$$C_P = C_0 \epsilon^{-\alpha} + C_1 \,, \tag{3.7}$$

where $\epsilon = (T - T_c)/T_c$. In accordance with (3.4) and (3.5) the amplitudes A_0 and C_0 are related by[32]

$$A_0 = C_0 \frac{\rho_c T_c'}{T_c} \,, \tag{3.8}$$

where ρ_c is the critical density. Density data for a critical mixture of 3-methylpentane plus nitroethane as a function of temperature have been reported by Greer and Hocken.[33] However, because of the weak character of the singular behavior of the thermal expansion coefficient, it is not possible to determine the coefficient A_0 from these data accurately,[34] while specific heat data for mixtures of 3-methylpentane plus nitroethane are currently not available. As an alternative we deduce the amplitudes A_0 and C_0 from the known asymptotic behavior of the correlation length through the relationship of two-scale-factor universality[35,36]

$$\xi_0\left[\frac{\alpha\rho_c C_0}{k_B}\right]^{1/3}=\xi_0\left[\frac{\alpha T_c A_0}{k_B T_c'}\right]^{1/3}=0.270\ . \tag{3.9}$$

Here k_B designates Boltzmann's constant and ξ_0 is the amplitude in the power law $\xi=\xi_0\epsilon^{-\nu}$ for the correlation length ξ. Evidence in support of the validity of two-scale-factor universality for classical fluids has been discussed elsewhere.[3] For the critical exponents α and ν we adopt the universal values[37] $\alpha=0.11$ and $\nu=0.630$ which satisfy the hyperscaling relation $3\nu=2-\alpha$. Noting that $\xi_0=(2.16\pm0.03)$ Å as determined by Chang *et al.*[8] and $\rho_c=0.7920$ g/cm^3 as measured by Greer and Hocken,[33] we obtain from (2.1) and (3.9)

$$A_0=(0.30\pm0.02)\times10^{-4}\ \mathrm{K}^{-1}\ , \tag{3.10}$$

$$C_0=(0.31\pm0.02)\ \mathrm{J/gK}\ . \tag{3.11}$$

From (3.6) and (3.10) it follows that the specific volume $V=\rho^{-1}$ should have an expansion of the form

$$\rho^{-1}=\rho_c^{-1}(1+R_0\epsilon^{1-\alpha}+R_1\epsilon) \tag{3.12}$$

with $R_0=A_0T_c/(1-\alpha)=0.0101\pm0.0006$. We have fitted (3.12) to the experimental density data reported by Greer and Hocken[33] with R_0 fixed at the value predicted from two-scale-factor universality. With the parameter values

$$\rho_c^{-1}=1.262\,62\ \mathrm{cm^3/g},$$

$$R_0=0.0101,\ R_1=0.385\ , \tag{3.13}$$

Eq. (3.12) reproduces the experimental density data with a standard deviation of 3×10^{-6} cm^3/g in the experimental temperature range

$$2\times10^{-4}\le\epsilon\le1.7\times10^{-2}\ . \tag{3.14}$$

For the slope of the data we thus recover the expansion (3.6),

$$\alpha_P=(0.030\epsilon^{-\alpha}+1.28)\times10^{-3}\ \mathrm{K}^{-1}\ . \tag{3.15}$$

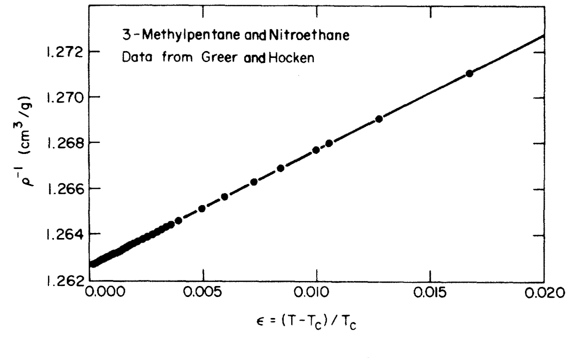

FIG. 8. Reciprocal density ρ^{-1} as a function of $\epsilon=(T-T_c)/T_c$ for 3-methylpentane plus nitroethane at the critical composition. Points represent the data obtained by Greer and Hocken (Ref. 33) and the curve corresponds to Eq. (3.11).

The experimental data for ρ^{-1} are shown in Fig. 8 as a function of the reduced temperature ϵ; the curve in this figure represents Eq. (3.12) with the parameter values (3.13). In practice,[34] Eq. (3.12) differs little from a linear function of ϵ. To elucidate the singular behavior of the thermal expansion coefficient we have made estimates of the slope $(\partial\rho^{-1}/\partial T)_P$ from piecewise linear fits to ten successive experimental data points for ρ^{-1} at various temperatures. The values thus deduced for α_P are shown in Fig. 9. The dashed curve indicates a constant value if all experimental data for ρ^{-1} are fitted to a linear equation[34]; the solid curve represents the expansion (3.15). From the fact that the slopes exhibit an upward curvature close to T_c we conclude that the experimental density data are consistent with the weak divergence of the thermal expansion coefficient predicted from two-scale-factor universality. We note, however, that the magnitude of the anomalous term as predicted by us is appreciably

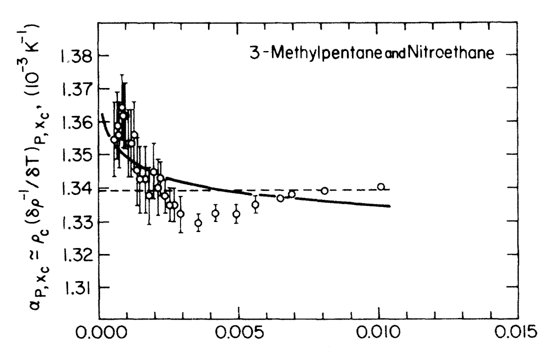

FIG. 9. Thermal expansion coefficient $\alpha_{P,x}$ of 3-methylpentane plus nitroethane at the critical composition $x=x_c$ as a function of $\epsilon=(T-T_c)/T_c$. Points represent values deduced by piecewise linear fits from the data of Greer and Hocken (Ref. 33). Dashed curve indicates an average constant value and the solid curve represents Eq. (3.14).

smaller[34] than originally suggested by Greer and Hocken.

From the identity [cf. (3.5)]

$$\rho_c C_P = \alpha_P T \Big/ \left(\frac{\partial T}{\partial P}\right)_S \tag{3.16}$$

and our experimental value (2.4) for $(\partial T/\partial P)_S$, combined with the value of α_P as deduced from the data of Greer and Hocken, we determine the value of the specific heat at $\Delta T = 45$ mK as

$$C_P = (2.48 \pm 0.07)\ \mathrm{J/gK}\ . \tag{3.17}$$

This result combined with (3.7) and (3.11) yields

$$C_1 = 1.66\ \mathrm{J/gK}\ ,$$

so that the temperature dependence of the specific heat is represented by

$$C_P = (0.31\epsilon^{-\alpha} + 1.66)\ \mathrm{J/gK}\ . \tag{3.18}$$

If we neglect any heat of mixing effects, we estimate the noncritical specific heat of an equimolar mixture of 3-methylpentane and nitroethane from the specific heat data for the pure components as[30]

$$C_P = (2.0 \pm 0.3)\ \mathrm{J/gK}\ .$$

It is interesting to note that Eq. (3.18) approaches this estimate at temperatures in the range $\epsilon \geq 0.1$ (i.e., $\Delta T \geq 30$ K).

Having determined the asymptotic behavior of the thermal expansion coefficient and the specific heat, we substitute (3.15) and (3.18) into (3.5) to calculate the slope of the adiabat as a function of temperature. The result is shown in Fig. 10. The coefficient $(\partial T/\partial P)_S$ changes significantly at temperatures very close to the critical temperature; it does approach the slope $T_c' = dT_c/dP$, but at temperatures many orders of magnitude too close to T_c to be accessible with our adiabatic cooling experiments.

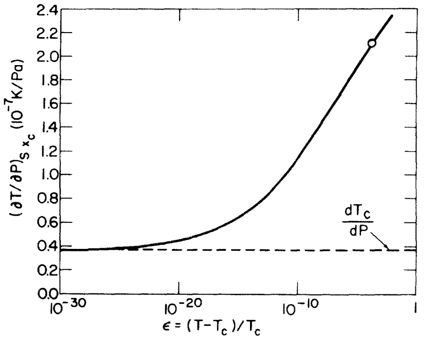

FIG. 10. Slope $(\partial T/\partial P)_{S,x}$ of the adiabat as a function of $\epsilon = (T - T_c)/T_c$ for 3-methylpentane plus nitroethane at the critical composition $x = x_c$. Datum point at $\epsilon = 1.5 \times 10^{-4}$ indicates the value (2.4) determined directly from our pressure quench experiments.

It is possible to make a nonlinear extrapolation of the experimental adiabat in Fig. 6 to zero pressure quench by taking into account the temperature dependence of the slope. We then estimate that the observed adiabat actually intersects the temperature axis at $\Delta T = -(1.1 \pm 0.5)$ mK. This result confirms that the temperature T_s at which, in our experiments, spinodal decomposition was observed, was close to, but slightly below, T_c.

B. Dimensionless adiabatic coupling constant

The basic thermodynamic quantity related to our spinodal decomposition measurements is the magnitude of the variation $\delta \Delta T = \delta[T - T_c(P)]$ as a result of an adiabatic pressure change δP. This same quantity was earlier considered by Ferrell and Bhattacharjee in their theoretical analysis of ultrasonic attenuation near the critical point.[19,20] From (3.2) and (3.3) we note that close to the critical point

$$\left(\frac{\partial \Delta T}{\partial P}\right)_S = \left(\frac{\partial T}{\partial P}\right)_S - T_c' = -\frac{T_c S_c'}{C_P}\ . \tag{3.19}$$

This result can be written in the form

$$\left(\frac{\partial \Delta T}{\partial P}\right)_S = -\frac{g}{\rho_c C_P}\ , \tag{3.20}$$

where

$$g = \rho_c T_c S_c' \tag{3.21}$$

is the adiabatic coupling constant introduced by Ferrell and Bhattacharjee.[19,20] This coupling constant g can be either positive or negative depending upon what happens upon a fast pressure quench. If, for a system with an upper critical solution point, g is positive, spinodal decomposition near the critical point is induced by a sudden increase of the pressure; if g is negative, as it is for 3-methylpentane plus nitroethane, spinodal decomposition is induced by a sudden decrease of the pressure.

The thermodynamic information presented above enables us to determine the coupling constant g for 3-methylpentane plus nitroethane. In particular, from (2.1), (2.4), (3.17), and (3.19) we obtain[38]

$$g = -0.34 \pm 0.01\ . \tag{3.22}$$

IV. CRITICAL ULTRASONIC ATTENUATION

Measurements of ultrasonic attenuation in a critical mixture of 3-methylpentane plus nitroethane as a function of temperature and frequency have recently been reported by Harada and Ishida.[39,40] At a given frequency the sound absorption coefficient attains its largest value at the critical temperature. For a quantitative analysis of the effect we decompose the sound attenuation coefficient α_s as

$$\alpha_s = \Delta\alpha_s + \bar{\alpha}_s \ . \tag{4.1}$$

Here $\bar{\alpha}_s$ represents the background absorption in the absence of critical fluctuations and $\Delta\alpha_s$ represents the additional increase in the sound absorption coefficient observed in the critical region.

A theory for the critical attenuation coefficient $\Delta\alpha_s$ has been formulated by two of the authors.[19,20] The theory uses the adiabatic temperature variation described by (3.20) and requires as a second ingredient an evaluation of the specific volume $V=\rho^{-1}$ as a function of P and ΔT. For this purpose we consider the relation $dG=-S\,dT+V\,dP$ for the thermodynamic potential G at constant $x=x_c$, so that, upon integration at constant P,

$$G(P,\Delta T)=G_c(P)-\int_0^{\Delta T} S(P,\Delta T)d\Delta T \ . \tag{4.2}$$

The specific volume V is then obtained as

$$V=\left[\frac{\partial G}{\partial P}\right]_T=\left[\frac{\partial G}{\partial P}\right]_{\Delta T}+\left[\frac{\partial G}{\partial \Delta T}\right]_P\left[\frac{\partial \Delta T}{\partial P}\right]_T$$

$$=G_c'-S_c'\Delta T+T_c'S \ , \tag{4.3}$$

where we have approximated the derivatives of G and S parallel to the critical line by their values on the critical line. The sound velocity is now obtained in the usual way from the adiabatic compressibility $-V^{-1}(\partial V/\partial P)_S$ with

$$\left[\frac{\partial V}{\partial P}\right]_S=G_c''+T_c'S-S_c''\Delta T-S_c'\left[\frac{\partial \Delta T}{\partial P}\right]_S \ . \tag{4.4}$$

Hence, the singular critical variation of the adiabatic compressibility is determined by the asymptotic behavior of $(\partial\Delta T/\partial P)_S$ that was discussed in Sec. III B. With the aid of (3.20) we thus obtain for the sound velocity u,

$$\frac{1}{u^2}=-\rho_c^2\left[\frac{\partial V}{\partial P}\right]_S\simeq\frac{1}{u_c^2}-\frac{g^2}{T_cC_P} \ , \tag{4.5}$$

where u_c is the sound velocity at the critical temperature. This result is analogous to the formula for the sound velocity of liquid helium in the vicinity of the λ point.[41] The sound velocity u can be generalized to a complex frequency-dependent sound velocity $\tilde{u}$. For this purpose we write Eq. (3.7) for the specific heat in the form $C_P=\Delta C+C_1$, where

$$\Delta C=C_0\epsilon^{-\alpha} \ , \tag{4.6}$$

and replace the singular part of the specific heat ΔC by a complex specific heat $\Delta\tilde{C}$. We thus obtain for the critical sound attenuation coefficient[42,43]

$$\Delta\alpha_s=\frac{2\pi}{\lambda}\frac{\mathrm{Im}(\tilde{u}^{-1})}{\mathrm{Re}(\tilde{u}^{-1})}\simeq\frac{\pi}{\lambda}\frac{\mathrm{Im}(\tilde{u}^{-2})}{\mathrm{Re}(\tilde{u}^{-2})}\simeq\frac{\pi}{\lambda}\frac{u_c^2g^2}{T_c}\left[\frac{\mathrm{Im}\Delta\tilde{C}}{\mathrm{Re}\Delta\tilde{C}}\right]\frac{\mathrm{Re}\Delta\tilde{C}}{(\mathrm{Re}\Delta\tilde{C}+C_1)^2} \ , \tag{4.7}$$

where λ is the wavelength of the ultrasound and where we have made use of the fact that $\Delta C \ll C_1$.

The principle of dynamic scaling allows us to determine the frequency dependence of $\tilde{C}_P$ at the critical temperature from the known temperature dependence of the thermodynamic specific heat C_P as discussed more fully elsewhere.[43] For this purpose we introduce a characteristic temperature-dependent relaxation rate γ proportional to $\epsilon^{z\nu}$, where $\nu=0.63$ is the critical exponent for the correlation length ξ and $z=3.06$ is the dynamic scaling exponent for the decay of the order-parameter fluctuations as determined by Burstyn and Sengers.[9] Thus, the thermodynamic critical behavior of the specific heat as expressed by (4.6) can be reexpressed as $\Delta C\propto\gamma^{-\alpha/z\nu}$. In passing to the critical point this relation goes over into the critical frequency dependence $\Delta\tilde{C}\propto(-i\omega)^{-\alpha/z\nu}$, from which it follows that

$$\frac{\mathrm{Im}\Delta\tilde{C}}{\mathrm{Re}\Delta\tilde{C}}=\tan\frac{\pi\alpha}{2z\nu}\simeq\frac{\pi\alpha}{2z\nu} \ . \tag{4.8}$$

A further simplification of (4.7) comes from the equality

$$\mathrm{Re}\Delta\tilde{C}(2\pi f)=\Delta C(\epsilon_f) \ , \tag{4.9}$$

which expresses the fact that for any given frequency $f=\omega/2\pi$ there exists an equivalent thermodynamic reduced temperature ϵ_f. By substituting (4.8) and (4.9) into (4.7) and noting that the experimental quantity reported by Ishida and Harada is α_s/f^2 and that $\lambda=u_c/f$, we rewrite (4.7) as

$$\lim_{T\to T_c}\frac{\Delta\alpha_s}{f^2}=\frac{\pi^2\alpha u_cg^2}{2z\nu T_cf}\frac{\Delta C(\epsilon_f)}{C_P^2(\epsilon_f)} \ , \tag{4.10}$$

where $\Delta C(\epsilon_f)$ is the singular part of the specific heat as given by (4.6).

Ishida and Harada[40] have reported measurements of α_s/f^2 for 3-methylpentane plus nitroethane as a function of temperature at a frequency $f = 6$ MHz. The data appear to approach the value

$$\alpha_s/f^2 \simeq (205 \pm 10) \times 10^{-16}\ \mathrm{s^2/cm}$$

at the critical temperature. From an analysis of preliminary attenuation data as a function of frequency[39] we estimate the background contribution to the sound attenuation as

$$\bar{\alpha}_s/f^2 = (7 \pm 1) \times 10^{-16}\ \mathrm{s^2/cm}$$

(see Refs. 19 and 30). Since this background contribution is only about 3% of the total attenuation coefficient, an accurate estimate of the background is not needed. We thus conclude from the work of Ishida and Harada[40] that

$$\lim_{T \to T_c} \frac{\Delta\alpha_s}{f^2} = (20 \pm 1) \times 10^{-15}\ \mathrm{s^2/cm}\quad (f = 6\ \mathrm{MHz})\ . \tag{4.11}$$

To make a comparison with the dynamic scaling theory we need to relate the frequency $f = 6$ MHz to the equivalent temperature difference ϵ_f. From an analysis of the extensive experimental information for ^{3}He near the critical point,[44] it is found that this relationship can be determined to a good approximation from the temperature dependence of $\Delta\alpha_s$ by identifying ϵ_f with $\epsilon_{1/2}$, where $\epsilon_{1/2}$ is the value of ϵ for which $\Delta\alpha_s$, at the given frequency f, is equal to one-half of its value at the critical temperature.[45] By invoking universality and applying this criterion to the data of Ishida and Harada we estimate $T - T_c \simeq 2.6$ K which corresponds to $\epsilon_f \simeq 8.7 \times 10^{-3}$. We found in (3.17) and (3.18) that at the lower temperature $\Delta T = 45$ mK, or $\epsilon = 1.5 \times 10^{-4}$, $C_P = 2.48$ J/gK, and $\Delta C = 0.82$ J/gK. The temperature $\epsilon_{1/2} \simeq 8.7 \times 10^{-3}$ now being larger by a factor of 58, we have to reduce ΔC by a factor of $(58)^{-\alpha} = 0.64$. Thus, ΔC and C_P both decrease by 0.29 J/gK, so that the values to be inserted into (4.10) for $f = 6$ MHz are

$$\Delta C(\epsilon_f) = 0.53\ \mathrm{J/gK}\ , \tag{4.12a}$$

$$C_P(\epsilon_f) = 2.19\ \mathrm{J/gK}\ . \tag{4.12b}$$

The sound velocity of 3-methylpentane plus nitroethane near the critical point has been measured by Kruer and Gammon.[46] From their data at 2 MHz we conclude $u_c = (1.0995 \pm 0.0002) \times 10^5$ cm/s, where the effect of the difference between 2 MHz and the frequency $f = 6$ MHz needed here is negligibly small. By substituting (4.12a) and (4.12b) and the information presented in Sec. III for g and C_P into (4.10) we predict

$$\lim_{T \to T_c} \frac{\Delta\alpha_s}{f^2} = (21 \pm 4) \times 10^{-5}\ \mathrm{s^2/cm} \tag{4.13}$$

in agreement with the experimental result (4.11). Alternatively, we can substitute the experimental value (4.11) into (4.10) and then solve the equation for the adiabatic coupling constant g. This procedure yields

$$|g| = 0.33 \pm 0.03 \tag{4.14}$$

in agreement with the value $g = -0.34 \pm 0.01$ found in Sec. II from the experimental thermodynamic data.

V. CONCLUSIONS

In this paper we have determined for 3-methylpentane plus nitroethane at the critical composition the rate of change of the critical temperature T_c with pressure and the slope of the adiabat in the P-T diagram. Combining our data with the density data of Greer and Hocken[33] we were able to determine the asymptotic critical behavior of the thermal expansion coefficient and of the specific heat consistent with two-scale-factor universality as well as the value of the adiabatic coupling constant which appears in the dynamic scaling theory of critical sound attenuation. With this theory our thermodynamic data were found to be in good agreement with the ultrasonic attenuation data of Ishida and Harada.[40]

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