PHYSICAL REVIEW E VOLUME 61, NUMBER 1 JANUARY 2000

Dynamic scaling of the critical ultrasonic attenuation in binary liquids: Evidence from broadband spectrometry

S. Z. Mirzaev,* T. Telgmann, and U. Kaatze†
Drittes Physikalisches Institut, Georg-August-Universität, Bürgerstrasse 42-44, D-37073 Göttingen, Germany

(Received 17 February 1998; revised manuscript received 4 August 1999)

Between 200 kHz and 500 MHz, the ultrasonic attenuation spectrum of the ethanol/dodecane mixture of critical composition has been measured at various temperatures near the critical one. The measured broadband spectra are evaluated in light of the Ferrell-Bhattacharjee dynamic scaling theory. The experimental findings largely fit the theoretical spectral function if suitable crossover corrections are made using dynamic light-scattering data. The measured scaling function follows the predictions of the recent Folk-Moser renormalization-group theory even better. Combining our ultrasonic attenuation coefficient data with density data from the literature, the asymptotic critical behavior of the thermal expansion coefficient and of the specific heat has been determined and found consistent with the two-scale factor universality. The sonic attenuation data have also been evaluated to yield the adiabatic coupling constant g of the dynamic scaling theory. The unusually small absolute value $|g|=0.1$ resulted, in fairly good agreement with $|g|=0.13$ as following from thermodynamic data.

PACS number(s): 62.60.+v, 64.60.Ht, 43.35.+d

I. INTRODUCTION

Within the framework of the Ferrell-Bhattacharjee dynamic scaling theory (FB, [1]), the sound attenuation per wavelength α_λ $(=\alpha\lambda)$ of a binary liquid, near its critical demixing temperature T_c, is given by

$$\alpha_\lambda = \pi A(t) u^2(f) F(\Omega). \tag{1}$$

Here α is the attenuation coefficient of a sonic wave with wavelength λ, f is the frequency, t and Ω are the reduced temperature and (angular) frequency, respectively, and u is the sound velocity. The assumption that α_λ can be represented by a simple product of a frequency-independent amplitude $A(t)$ and a scaling function depending only on Ω is known as the dynamic scaling hypothesis for the acoustical anomaly at a critical point [2,3]. In their theoretical treatment, Tanaka and Wada [4] argued that the critical amplitude may also (slightly) depend on the frequency. Consequently, the dynamic scaling hypothesis might not be unequivocally applied to any acoustical anomaly near a critical demixing point. On the other hand, experimental results seem to indicate that the dynamic scaling theory for a binary liquid mixture of critical composition applies adequately for the ultrasonic attenuation as a function of frequency and temperature [5,6]. Unfortunately, in those experimental studies just a comparatively small frequency range had been covered. Hence the significance of the measured spectra is limited. We thus measured, for the ethanol/dodecane system near its consolute point, ultrasonic attenuation data over the wide frequency band from 0.2 to 500 MHz, in order to analyze the spectra in light of the dynamic scaling model. With many binary mixtures, additional contributions from noncritical relaxation processes may disturb the sonic attenuation spectra [7]. For this reason we have chosen the ethanol/dodecane system here. Ethanol does not show relaxational characteristics at frequencies between 100 kHz and 2 GHz [8]. Dodecane exhibits indeed a relaxation process within that frequency range [9]. The relaxation time, however, is $\tau=120$ ps at 25 °C, corresponding with a relaxation frequency $(2\pi\tau)^{-1}=1.3$ GHz above our frequency range of measurement. Hence in the present measurements no relaxation mechanisms of the constituents are expected to contribute to the ultrasonic attenuation spectra.

II. FERRELL-BHATTACHARJEE THEORY

For a comparison with measured broadband sonic spectra, let us consider the scaling theory in some more detail. The critical contribution α^c to the acoustic attenuation coefficient α at the critical temperature is related to the complex heat capacity $\tilde{C}_P$ according to [1]

$$\alpha^c(\omega,T_c) \propto \omega\,\mathrm{Im}[\tilde{C}_P(\omega)]^{-1} \approx \frac{\delta\pi\omega^2}{2[\mathrm{Re}\,\tilde{C}_P(t_f)]^2}\left[\frac{\Omega_{1/2}}{\omega}\right]^{1+\delta}, \tag{2}$$

where $\delta=\alpha_0/(Z_0\nu)$, $\omega=2\pi f$, and α_0, Z_0, as well as ν are the specific-heat critical exponent, the dynamical critical exponent, and the critical exponent of the correlation length of the order-parameter fluctuations, respectively. Parameter

$$\Omega_{1/2}=(\omega/\omega_0)t_f^{-Z_0\nu} \tag{3}$$

is the dimensionless half-attenuation frequency. In the original theory [10] it was named a and a value of 2.67 was predicted for this parameter [Eq. (B13) in Ref. [1]]. In the above relations t_f is a characteristic reduced temperature [6] and $\omega_0=k_BT/3\pi\eta_0\xi_0^3$, with k_B denoting Boltzmann's constant and with the viscosity amplitude η_0 and the amplitude ξ_0 of the correlation length. Following the treatment given in

---

*Permanent address: Heat Physics Department, Uzbek Academy of Sciences, Katartal 28, Tashkent 700135, Uzbekistan.

†Electronic address: uka@physik3.gwdg.de

1063-651X/2000/61(1)/542(8)/$15.00

the literature [10], the attenuation per wavelength can be written as

$$\alpha_\lambda^c(\omega,T)=\alpha_\lambda^c(\omega,T_c)F(\Omega). \tag{4}$$

Herein, $\alpha_\lambda^c(\omega,T_c)$ is the attenuation per wavelength near the critical temperature T_c and $F(\Omega)$ is a scaling function [10],

$$F(\Omega)=\frac{3}{\pi}\int_0^\infty \frac{x\,dx}{(1+x)^2}\,\frac{\Omega x(1+x)^{1/2}}{x^2(1+x)+\Omega^2}. \tag{5}$$

The reduced frequency may be expressed as $\Omega=\omega/\omega_D$, where $\omega_D=2D\xi^{-2}$ is the relaxation frequency characterizing the diffusion of local energy fluctuations. D is the mutual diffusion coefficient and ξ the correlation length. Both quantities are related to another according to the suggestive equation [11,12]

$$D=k_BT/(6\pi\eta\xi). \tag{6}$$

Taking into account the dependences of η and ξ from the reduced temperature, $\eta=\eta_0t^{-(Z_0-3)\nu}$ and $\xi=\xi_0t^{-\nu}$, respectively, one gets

$$\Omega=3\pi\eta_0\xi_0^3\omega t^{-Z_0\nu}/(k_BT)=(\omega/\omega_0)t^{-Z_0\nu}. \tag{7}$$

According to Ferrell and Bhattacharjee, the sonic attenuation at the critical point can be represented by

$$\alpha(\omega,T_c)/f^2=\frac{\pi^2\delta\Delta C(t_f)}{2T_c}\left(\frac{\Omega_{1/2}\omega_0}{2\pi}\right)^\delta\frac{u_cg^2}{C_0^2(t_f)}f^{-(1+\delta)}+B. \tag{8}$$

Herein, $\Delta C(t_f)$ is the critical amplitude describing the singular behavior [13] of the heat capacity $C_P=\mathrm{Re}(\tilde{C}_P)=\Delta Ct^{-\alpha_0}+C_0$, u_c is the sound velocity at T_c, B is a frequency-independent noncritical background contribution to α/f^2, and g is the adiabatic coupling constant which, according to

$$g=\rho_cC_P\left(\frac{dT_c}{dP}-\frac{T\alpha_P}{\rho C_P}\right), \tag{9}$$

is related to the density ρ_c of the mixture at T_c and the thermal expansion coefficient α_P at constant pressure. The Ferrell-Bhattacharjee theory is based on the assumption that ΔC is very small as compared to C_0. For the ethanol/dodecane system this precondition is clearly fulfilled since $\Delta C/C_0=0.035$ (see below).

Using the well-known $\delta=0.06$, Eq. (8) has been rewritten to yield the form [6,14]

$$\alpha(\omega,T_c)/f^2=S(\omega,t_f)f^{-1.06}+B \tag{10}$$

with an amplitude $S(\omega,t_f)$ which is predicted theoretically to (weakly) depend upon frequency. Equation (10) is frequently used in the evaluation of experimental data. It will be discussed in detail below. Considering Eqs. (4)–(8) and using a more recent form of the scaling function yields an empirical attenuation function [1]

$$\alpha_\lambda^c(\omega,T)/\alpha_\lambda^c(\omega,T_c)=F_{\mathrm{FB}}(\Omega), \tag{11}$$

where

$$\begin{aligned}F_{\mathrm{FB}}(\Omega)&=[1+0.414(\Omega_{1/2}/\Omega)^{1/2}]^{-2}\\&=[1+0.414(t/t_f)^{0.964}]^{-2}.\end{aligned} \tag{12}$$

Here $\Omega_{1/2}$ is the value of the scaled frequency Ω at 50% attenuation as mentioned before.

Taking relation $\alpha_\lambda^c(\omega,T_c)=S(\omega,t_f)uf^{-0.06}$ into account and neglecting any prospective frequency dependence in the amplitude function $[S(\omega,t_f)=S(t_f)]$ here, Eq. (4) finally reads

$$\alpha_\lambda^c(\omega,T)=S(t_f)uf^{-0.06}F_{\mathrm{FB}}(\Omega). \tag{13}$$

This relation enables an easy representation of the frequency-dependent ultrasonic attenuation.

III. EXPERIMENT

For a comparison of the theoretical predictions with measured sonic spectra, we investigated the ethanol/dodecane system which exhibits an upper critical solution temperature (UCST). Various samples have been prepared using ethanol ($>99.8\%$) and *n*-dodecane ($>99\%$) from Merck (Darmstadt, Germany). The critical parameters have been derived from mixtures of different composition X by monitoring the appearance of the meniscus when slowly cooling the sample. We found a critical temperature $T_c=(13.55\pm0.05)\,°\mathrm{C}$ for the critical mixture with mole fraction $X_c=0.687$ of ethanol. The UCST of our mixture was somewhat higher than the value given by Francis [15], but it was in good agreement with the data reported by Orzechowski [16]. The ultrasonic spectra have been measured for the solution of critical composition X_c in the homogeneous phase ($T>$UCST) at eight reduced temperatures t, $4.5\times10^{-4}\leqslant t\leqslant3.9\times10^{-2}$, mostly between 200 kHz and 500 MHz. We used two different methods and four different specimen cells to cover the frequency range. At $f<15$ MHz, a resonator method was appropriate in which the attenuation coefficient α relative to that of a carefully matched reference liquid was determined [17,18]. At $f\geqslant15$ MHz, a pulse-modulated wave transmission technique, in which the sample length is significantly varied, enabled absolute measurements of α [19]. The temperature of all specimen cells was controlled (and measured) to within 0.03 K. The error in the attenuation data was smaller than 5% at $f<15$ MHz and smaller than 1.5% at $f\geqslant15$ MHz.

IV. RESULTS AND DISCUSSION

Two different runs of ultrasonic attenuation coefficient measurements have been performed for the ethanol/dodecane mixture of critical composition. The first run covered the frequency range from 0.2 to 500 MHz; the second was mainly focused on the lower part of this range ($0.2\leqslant f\leqslant1.7$ MHz). In addition to the latter measurements, some data have been taken at $t=4.5\times10^{-4}$ and $f>100$ MHz in order to determine the B value [Eq. (8)] of the mixture. The low-frequency data from the second run are displayed in Table I. For two temperatures apart from the critical one, a plot of the complete attenuation spectra, in the format α/f^2

TABLE I. Attenuation coefficient per f^2 as a function of frequency as measured with a plano-concave resonator cell between 0.24 and 1.7 MHz displayed for an ethanol/dodecane mixture of critical composition at eight reduced temperatures t.

f (MHz)	α/f^2 (10^{-15} s^2/m)	f (MHz)	α/f^2 (10^{-15} s^2/m)	f (MHz)	α/f^2 (10^{-15} s^2/m)	f (MHz)	α/f^2 (10^{-15} s^2/m)
$t=4.5\times10^{-4}$				$t=1.29\times10^{-2}$			
0.24232	1487	0.78729	476	0.30654	591	0.7778	324
0.31031	1106	0.82112	460	0.34018	560	0.8113	315
0.34436	1002	0.85478	445	0.37385	521	0.8446	309
0.37844	918	1.37200	299	0.40753	495	1.3218	225
0.41253	848	1.40610	291	0.44122	472	1.3555	225
0.44663	789	1.44020	286	0.47492	452	1.3891	222
0.48074	739	1.47430	281	0.50861	431	1.4228	217
0.51485	693	1.50840	275	0.67706	341	1.4565	215
0.65128	528	1.54250	271	0.71070	345	1.5239	209
0.68534	544	1.57660	266	0.74429	332	1.5913	204
0.71937	509	1.61070	261				
0.75336	494	1.67890	253				
$t=3.43\times10^{-3}$		0.7851	440	$t=2.28\times10^{-2}$			
0.3094	963	0.8189	425	0.30366	399	0.8037	254
0.3434	876	1.2666	298	0.33698	377	0.8368	250
0.3774	811	1.3344	287	0.37033	371	1.3094	194
0.4114	753	1.3683	283	0.40369	354	1.3427	193
0.4454	707	1.4363	272	0.43707	344	1.3760	193
0.4794	667	1.4703	267	0.47045	333	1.4094	190
0.5134	626	1.5044	263	0.50383	322	1.4427	188
0.6495	492	1.5384	257	0.53721	311	1.4761	185
0.6834	494	1.5724	255	0.70402	276	1.5095	184
0.7174	468	1.6064	249	0.73732	262	1.5429	181
0.7513	454	1.6404	243	0.77057	259	1.5763	181
						1.6096	178
$t=6.79\times10^{-3}$		0.7489	412	$t=2.93\times10^{-2}$		0.8643	207
0.3084	813	0.7827	400	0.3017	304	1.3012	165
0.3423	748	0.8163	387	0.3348	292	1.3343	171
0.3762	697	0.8498	376	0.3680	285	1.3674	169
0.4101	654	1.3979	260	0.4011	279	1.4005	168
0.4440	617	1.4318	256	0.4343	273	1.4337	166
0.4779	583	1.4657	251	0.4675	265	1.4669	164
0.5118	553	1.4996	248	0.5006	261	1.5000	163
0.6474	431	1.5335	245	0.5338	252	1.5332	161
0.6813	433	1.5674	241	0.6996	224	1.5664	159
0.7151	422	1.6691	229	0.7327	219	1.5996	159
				0.7657	218	1.6327	156
				0.7987	213	1.6658	156
				0.8316	210	1.6989	151
$t=9.94\times10^{-3}$				$t=3.91\times10^{-2}$		0.8239	168
0.30752	691	0.8138	353	0.29891	209	0.8563	166
0.34127	641	0.8472	344	0.33171	205	1.3546	142
0.37504	605	1.3260	252	0.36454	207	1.3874	141
0.40883	569	1.3598	248	0.39739	203	1.4202	139
0.44263	540	1.3935	244	0.43024	202	1.4531	138
0.47643	515	1.4611	236	0.46310	197	1.4859	137
0.51024	491	1.4949	232	0.49596	196	1.5188	136
0.64547	391	1.5288	229	0.52882	191	1.5517	135
0.67922	384	1.5626	226	0.69308	175	1.5845	135
0.71295	382	1.5964	223	0.72587	172	1.6174	132
0.74665	372	1.6301	220	0.75862	173	1.6502	132
0.78030	363	1.6976	218	0.79131	169	1.6830	131

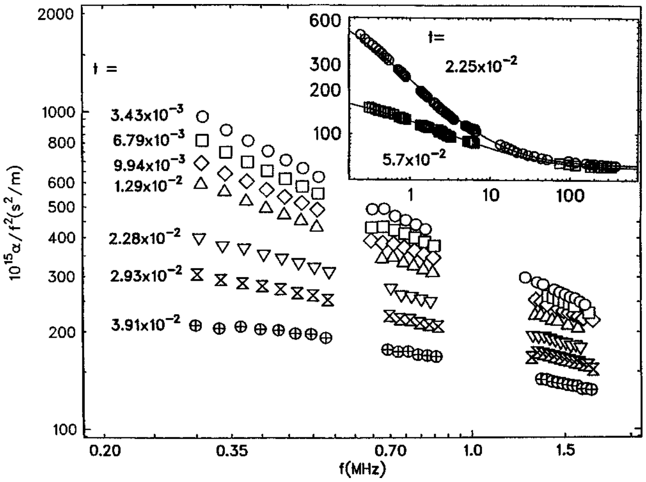

FIG. 1. Ultrasonic attenuation spectra at several reduced temperatures t for the ethanol/n-dodecane mixture of critical composition.

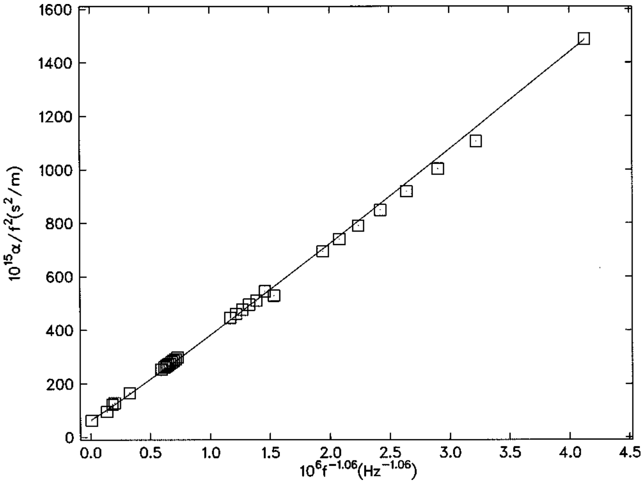

FIG. 2. The attenuation coefficient of the ethanol/n-dodecane mixture of critical composition at $t=1.36\times10^{-3}$ in the format α/f^2 plotted as a function of $f^{-1.06}$.

versus f, is given in the inset of Fig. 1. The spectra differ from each other predominantly at low frequencies. For this reason a series of spectra at several temperatures of measurement is displayed for the lower-frequency range ($f<2$ MHz) in the principal part of that figure. In conformity with the theoretical predictions, the data tend to increase with decreasing frequency and reduced temperature.

Each run of measurements was started at a temperature T well above the critical one in order to approach T_c by small steps afterwards. The critical temperature of the sample within a cell has been carefully determined by monitoring at every frequency of measurement the sound velocity u of the liquid mixture. Distinct changes in u occurred at the onset of phase separation. We were thus able to determine the critical temperature of the ethanol/dodecane mixture under examination to within 30 mK. These T_c measurements have been verified by visual observations of the appearance of the meniscus.

A value $T_c=15.55\,^\circ\mathrm{C}$ has been observed in the second run of sound attenuation measurements. It differs by 2 K from the critical temperature determined by the aforementioned cloud point observations and light-scattering measurements in which freshly prepared samples were used. This discrepancy is taken to be due to water uptake of the sample liquids as the ultrasonic measuring cells were not hermetically sealed. We studied the effect of small amounts of water in the critical temperature of the ethanol/dodecane mixture of critical composition independently, using optical methods [23]. On addition of 0.02% w/w of water, we found T_c to increase by 3.5 K. Near T_c, however, the characteristic angular frequency $\omega_o=2D_0/\xi_0^2$ of concentration fluctuations in the mixture with water added had the same value as in the pure sample. We conclude that small amounts of water do not significantly change the kinetics of concentration fluctuations in the binary mixture at constant t.

Let us start our inspection of the dynamic scaling theory with an examination of the frequency dependence of the critical sound attenuation. Figure 2 shows a plot of $\alpha(\omega,T_c)/f^2$ as a function of $f^{-1.06}$. The data can be well represented by a straight line as following from Eq. (10) if the frequency dependence in S can be neglected. The slope of the line yields $S=7.24\times10^{-7}$ $\mathrm{s}^{0.94}/\mathrm{m}$. From the intercept it follows that $B=64\times10^{-15}$ s^2/m.

When analyzing the measured ultrasonic attenuation data in terms of the dynamic scaling theory [1], difficulties arose from the indefiniteness of the temperature interval in which the theoretical predictions might apply. On the one hand, Eq. (10) has been derived for temperatures close to T_c only and we do not know the range of t values up to which the applicability of the theory can be extended. On the other hand, in order to reach a high accuracy in the temperature dependence of the sonic attenuation spectra, measurements have been conducted over a broad range of t values. For such broad t ranges, it will be necessary to introduce crossover corrections to clearly reveal the underlying universal scaling characteristics. Recently, Bhattacharjee and Ferrell presented a simple correction procedure [26] that will be applied in the following discussion of the ultrasonic attenuation spectra. This procedure is based on the use of an effective reduced temperature $\tilde{t}=(T_c-\tilde{T})/T_c$, which according to the equation

$$\tilde{t}=t[1+\beta(\kappa/q_c)]^{1/2} \tag{14}$$

is related to the reduced temperature t. In the crossover correlation factor $[1+\beta(\kappa/q_c)]^{1/2}$, parameter $\beta=1.18$ [26], $\kappa=\xi^{-1}=\xi_0^{-1}t^{0.63}$, and q_c is the characteristic noncritical crossover wave number. Rayleigh linewidth measurements yield $\xi_0=3.4$ Å for the ethanol/dodecane system if $T_c=13.55\,^\circ\mathrm{C}$ is used. Hence $\kappa=2.94\times10^9$ m^{-1} $\mathrm{t}^{0.63}$. The value for q_c has been derived from dynamic light-scattering data [23] yielding the relaxation rate $\gamma(q,\kappa)$ that may be expressed as

$$\gamma(q,\kappa)=q^2D(q,\kappa)=q^2D_0r(1+r/q_c), \tag{15}$$

where q is the wave vector, $r=(q^2+\kappa^2)^{1/2}$, and $D_0=k_BT/(6\pi\eta)$ [26]. Fitting the $\gamma(q,\kappa)$ data from the measurements to relation (15) yields $q_c=1.38\times10^9$ m^{-1} and the $\tilde{t}$ values given in Table II. As expected intuitively, close to $T_c,\tilde{t}\approx t$ holds whereas noticeable crossover corrections

TABLE II. Reduced temperatures t and effective values $\tilde{t}$ used in crossover corrections, as well as the sound velocity u and frequency-independent background attenuation B of the ethanol/dodecane mixture of critical composition.

t 10^{-3}	$\tilde{t}$ 10^{-3}	u m/s	B 10^{-15} s^2/m
0.45	0.454	1244.77	64
3.43	3.55	1241.41	63
6.79	7.15	1237.45	62
9.94	10.6	1233.67	61.5
12.9	13.9	1229.67	61
22.8	25.3	1218.04	59
29.3	33.0	1210.37	58
39.1	45.0	1198.97	57

emerge at larger t values. In the following analysis of the ultrasonic attenuation spectra, the effective reduced temperature values will be used.

For a more definite comparison of the FB theory with the measured ultrasonic data, it is necessary to calculate the parameters S and g [Eqs. (9) and (10)] from thermodynamic data of independent experiments. Since suitable calorimetric and light-scattering data are not available for the ethanol/dodecane system, we used the following well-known routines [14] to obtain the required parameters. Within the temperature range $0.1\ \mathrm{K} \leqslant T - T_c \leqslant 10\ \mathrm{K}$, the background part C_0 of the heat capacity of the binary mixture, with an error of less than 5%, can be approximated assuming an ideal mixing behavior,

$$C_0 = XC_1 + (1-X)C_2, \tag{16}$$

where X is the mole fraction of ethanol and C_1 and C_2 are the heat capacity [21,22] of ethanol and of dodecane, respectively. The amplitude ΔC in the singular part of the heat capacity can be derived from the two-scale factor universality [14]

$$\xi_0 [\alpha_0 \rho_c \Delta C / k_B]^{1/3} = 0.27, \tag{17}$$

which relates ΔC to the correlation length parameter ξ_0 of local concentration fluctuations and to the density ρ_c of the critical mixture at T_c. In Eq. (17), α_0 is the critical exponent of the specific heat at constant pressure. In the homogeneous phase, the temperature dependence of the density $\rho(X_c, T)$ of the ethanol/dodecane mixture of critical composition is given by the linear relation [16]

$$\rho = 0.7768\ \ \mathrm{g\,cm^{-3}} - 8.09\times 10^{-4}\mathrm{g\,cm^{-3}\,K^{-1}} \times (T - 273.14\ \ \mathrm{K}). \tag{18}$$

With these assumptions, $C_0 = 2330\ \mathrm{J\,kg^{-3}\,K^{-1}}$ and $\Delta C = 82\ \mathrm{J\,kg^{-3}\,K^{-1}}$ follows for the system under consideration.

The pressure dependence of T_c can be considered by the differential quotient [20]

$$\left(\frac{dT_c}{dP}\right)_{\mathrm{crit}} = \frac{T_c \alpha_{pc}}{\rho_c \Delta C}, \tag{19}$$

where ''crit'' indicates the derivative along the critical line and α_{pc} is the singular part of the thermal expansion coefficient $\alpha_p = \rho[\delta\rho^{-1}/\delta T]_p$, given by the relation

$$\alpha_p = \alpha_{pc} t^{-\alpha} + \alpha_{pb}. \tag{20}$$

In Eq. (20), α_{pb} denotes the (noncritical) background part of α_p. Because of the weak singular behavior of the thermal expansion coefficient, however, it is impossible to accurately determine both parts, α_{pc} and α_{pb}, from density data. Alternatively, we derived α_{pb} of the mixture from a linear interpolation of the values of the constituents. Using $\alpha_p = 1.096 \times 10^{-3}\ \mathrm{K^{-1}}$ and $9.74\times 10^{-4}\ \mathrm{K^{-1}}$ for ethanol and dodecane at 25 °C [21], respectively, $\alpha_{pb} = 1.06\times 10^{-3}\ \mathrm{K^{-1}}$ is obtained for the critical mixture. Using recent density data from the literature [16], α_p has been calculated at various temperatures. From these data, along with the above value for α_{pb}, $\alpha_{pc} = 2.2\times 10^{-5}\ \mathrm{K^{-1}}$ follows. Using these data, $(dT_c/dP)_{\mathrm{crit}} = 10^{-7}$ K/Pa [Eq. (19)] and $g = -0.13$ [Eq. (9)] results $[\alpha_p = 1.11\times 10^{-3}\ \mathrm{K^{-1}}, C_p = 2527\ \mathrm{J\,kg^{-1}\,K^{-1}}, \rho_c = 764.2\ \mathrm{kg\,m^{-3}}, (T - T_c) = 0.1\ \mathrm{K}]$. The coupling constant g can be either positive or negative, depending on the response of the sample to a fast pressure change. The negative g for the mixture with the upper critical solution point means that a decrease in the pressure leads to spinodal decomposition of the binary liquid. Utilizing a falling ball viscosimeter, we have measured the shear viscosity $\eta(X_c, t)$ of the mixture of critical composition as a function of temperature and we fitted the data to the relation

$$\eta = \eta_0 t^{-0.0378} \tag{21}$$

in order to find the value of the parameter η_0. At $0 \leqslant t \leqslant 1.5\times 10^{-2}$, the viscosity parameter $\eta_0 = (1.25 \pm 0.01) \times 10^{-3}$ Pa s follows. Along with the result for ξ_0 ($= 3.4$ Å), the value for η_0 allows the characteristic angular frequency ω_0 in Eq. (8) to be calculated, using Eq. (7) in the form $\omega_0 = k_B T / 3\pi \eta_0 \xi_0^3$. We found $\omega_0 = 8.6\times 10^9\ \mathrm{s^{-1}}$, which is indeed a reasonable value $[\omega_0/(2\pi) = 1.4\ \mathrm{GHz}]$. In the following, this ω_0 value will be compared to the one which, according to Eqs. (11)–(13), can be derived from the broadband ultrasonic attenuation spectra.

Let us now focus on a comparison of the measured spectra with the predictions from the dynamic scaling theory. For this purpose it is useful to first determine, for every frequency f in a relevant frequency range, the corresponding characteristic reduced temperature t_f [6,14] in the expression for the dimensionless quantity $\Omega_{1/2}$ in Eqs. (2) and (8). It is known from the literature [1,6] that t_f can be well approximated by the t value at which, for a given f, α^c adopts one-half its value at T_c. The values of t_f for each measuring frequency of this study have been obtained in the following way.

If, for appropriate crossover correction, $\tilde{t}$ is used instead of t, Eqs. (11) and (12) predict the plot of $[\alpha_\lambda(\omega, \tilde{T})]^{-1/2}$ versus $\tilde{t}^{0.964}$ to define a straight line for each frequency f of measurement. Due to the resonator method used in this study, the f values slightly vary with temperature (Table I). We therefore interpolated the measured α-versus-f relation at every temperature of measurement to be able to consider the attenuation data at mean frequency values (close to the

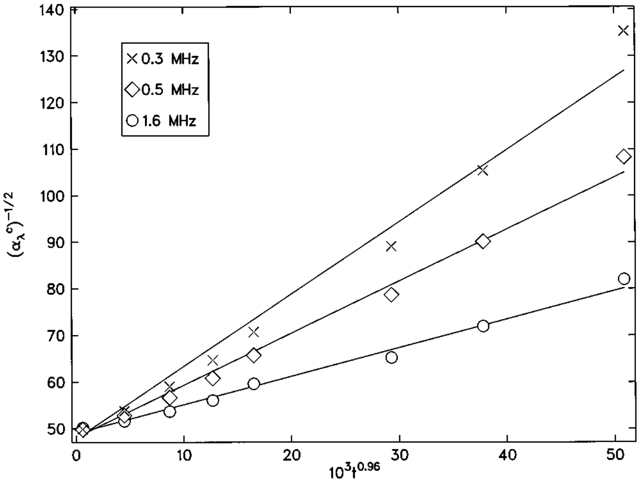

FIG. 3. Plot of $(\alpha_\lambda^c)^{-1/2}$ vs $\tilde{t}^{0.964}$ for the ethanol/dodecane data at three frequencies of measurements. Here $\alpha_\lambda^c = \alpha\lambda - Buf$, where $\alpha\lambda$ denotes the measured total attenuation per wavelength and Buf the background contribution.

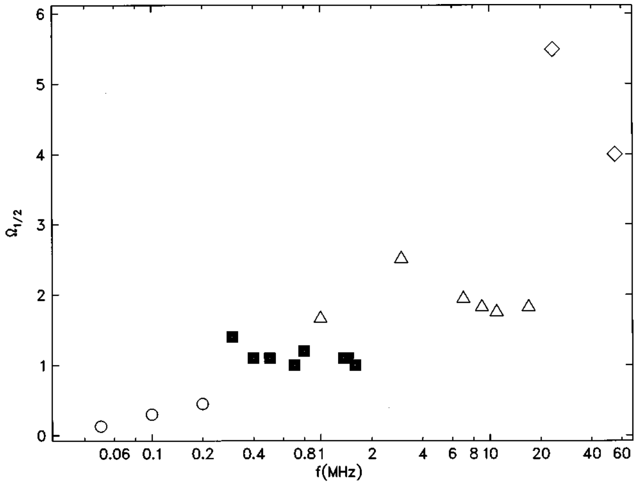

FIG. 4. The half-attenuation frequency $\Omega_{1/2}$ [Eq. (3)] as a function of measuring frequency f for the ethanol/dodecane mixture (full squares) as well as for the system trimethylpentane/nitroethane (triangles [6]) and nitrobenzene/hexane (circles [24], diamonds [25]). The literature data given in this plot have not been corrected for crossover effects.

measuring frequency) here. For three frequencies the dependence of the $\alpha_\lambda(\omega,T)$ data upon the effective reduced temperature is shown in Fig. 3. The $\alpha_\lambda(\omega,T)$ values have been derived from the measured $\alpha\lambda$ by simply subtracting the background contribution $Buf=(\alpha/f^2)_{f\to\infty}uf$, using α/f^2 values as measured at $f>100$ MHz. Fitting these $\alpha_\lambda(\omega,T)$ data to the analytical expressions [Eqs. (11) and (12)] yields $\alpha_\lambda^c(\omega,T_c)=4.2\times10^{-4}, 4.2\times10^{-4}$, and 4.0×10^{-4} at 0.3, 0.5, and 1.6 MHz, respectively. For these three frequencies, the corresponding quantity as measured at $t=4.5\times10^{-4}$ is almost constant: $\alpha\lambda - Buf = 4.0\times10^{-4}$. Hence in the critical contribution to the attenuation coefficient, the difference between the values predicted by Eqs. (11) and (12) using crossover corrections and the values measured close to T_c does not exceed 5%.

For eight frequencies of measurement, the half-attenuation values $\tilde{t}_f$ have also been obtained from the fit of the experimental $\alpha_\lambda(\omega,T)$ data to the theoretically predicted dependence of the attenuation per wavelength upon $\tilde{t}$. Utilizing these $\tilde{t}_f$ values and using $\omega_0=8.6\times10^9$ s^{-1}, the half-attenuation frequency $\Omega_{1/2}$ [Eq. (3)] has been calculated for the eight runs. The resulting $\Omega_{1/2}$ values are shown in Fig. 4, where $\Omega_{1/2}$ data from previous results for the systems 3-methylpentane/nitroethane [6] and nitrobenzene/hexane [24,25] are also presented. There seems to exist an overall tendency of the $\Omega_{1/2}$ values to increase with f. Notice, however, that we do not know the noncritical crossover wave numbers q_c [Eq. (15)] for the literature spectra. Therefore, no crossover corrections have been applied to the 3-methylpentane/nitroethane and the nitrobenzene/hexane data. Such corrections could change the $\Omega_{1/2}$ values at high frequencies ($f>1$ MHz) noticeably. Nonconstancy of the half-attenuation frequency values in Fig. 4 should thus not be overemphasized.

For an inspection of the FB scaling function, let us now consider the frequency dependence in our ultrasonic attenuation data (Fig. 1). In order to find the contribution $\alpha_\lambda(\omega,T)$ that is due to concentration fluctuations, we again subtracted from the measured attenuation per wavelength the background part Buf as found by measurements at $f>100$ MHz. The B values are given in Table II. We now fitted, at the same time, all experimental excess attenuation spectra $\alpha\lambda - Buf$ to Eq. (11). Relation (7) was used to calculate the reduced angular frequency Ω as a function of reduced temperature. In this evaluation of spectra, ω_0 was treated as an adjustable parameter. We found $\omega_0=4.4\times10^9$ s^{-1}. A more detailed comparison of this value from the sonic spectra with light-scattering data is given elsewhere [23]. We suppose the discrepancy between the two differently determined values to be predominantly due to the weak dependence of the scaling function upon the reduced frequency. Using $\omega_0=4.4\times10^9$ s^{-1} as derived from the ultrasonic spectra and assuming ΔC and C_p to only weakly depend on t_f, the amount of the coupling constant, g can be calculated from the slope S of the α/f^2-versus-$f^{-1.06}$ plot in Fig. 2. According to Eq. (8),

$$|g|=\left[S\,\frac{2T_cC_0^2}{\pi^2\delta u\Delta C}\left(\frac{2\pi}{\omega_0\Omega_{1/2}}\right)^{\delta}\right]^{1/2} \tag{22}$$

with $S=6.92\times10^{-7}$ s$^{0.94}$ m^{-1}, $u=1244.77$ ms^{-1}, $\Delta C=82$ J kg^{-1} K^{-1},$C_0=2320$ J kg^{-1} K^{-1}, and $\Omega_{1/2}=1.2$; $|g|=0.10\pm0.03$ follows, in fairly good agreement with $|g|=0.13$ as derived from Eq. (9). This agreement in the $|g|$ values determined from the ultrasonic spectra on the one hand and from thermodynamic data on the other hand may be taken to indicate the consistency of the theoretical conception underlying the evaluation of the ultrasonic attenuation data of the mixture of critical composition. We just briefly mention that, to our knowledge, $|g|=0.1$ is the smallest value reported for the adiabatic coupling constant. This small value correlates with the small critical contribution to the acoustic attenuation spectrum of the ethanol/dodecane system.

In Fig. 5, plots of $\alpha^c(T)/\alpha^c(T_c)=(\alpha-Bf^2)/\alpha^c(T_c)$ versus Ω are shown. Also given is the graph of the scaling

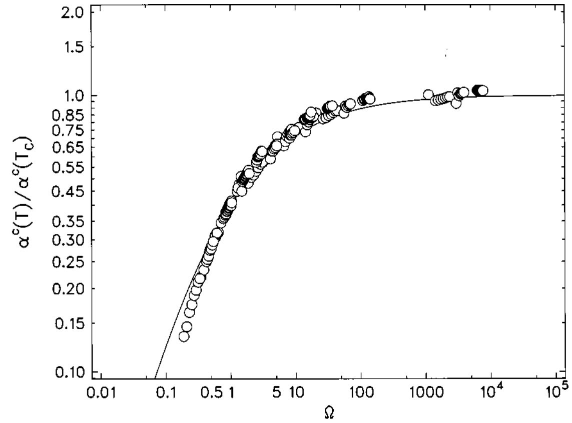

FIG. 5. Normalized attenuation coefficient per wavelength excluding the background contribution, $\alpha^c(T)/\alpha^c(T_c)$, bilogarithmically displayed as function of reduced frequency Ω. The curve is the graph of the empirical scaling function $F_{\rm FB}$ defined by Eq. (12). Experimental data have been taken for frequencies up to 1.7 MHz. The error in the experimental data is in the order of the symbols.

function defined by Eq. (12). At high frequencies and apart from the critical temperature, the background attenuation dominates the critical one. Therefore, the high-frequency excess absorption data are subject to somewhat elevated errors and are omitted from the diagram. But those data have been particularly used to determine the background contribution to the spectra. A log/log plot is given in order to accentuate the data at small Ω. Our excess absorption data at $f<1.7$ MHz display a good agreement with the empirical scaling function $F_{\rm FB}(\Omega)$ by Ferrell and Bhattacharjee [Eq. (12)], but at small Ω the measured data are somewhat smaller than predicted by $F_{\rm FB}(\Omega)$. The slope of the data at small Ω is equal to one which, within the framework of the Ferrell-Bhattacharjee model, is expected only in the extreme limit of vanishing reduced frequency. This apparent anomaly corresponds with the upwards curvature of the 0.3 MHz data in Fig. 3. These findings might reflect a frequency dependence in the critical amplitude $A(t)$ at small frequencies, as theoretically predicted by Tanaka and Wada [4]. In recent years, however, theoretical improvements have been achieved by various authors [27–32]. Rather interesting, at $\Omega<1$ the recent nonasymptotic scaling function suggested by the Folk-Moser renormalization-group theory predicts $\alpha^c(T)/\alpha^c(T_c)$ values smaller than those found in our measurements (Fig. 6). At larger distance from criticality $(10<\Omega<500)$, the Folk-Moser scaling function $F_{\rm FM}$ appears to be superior to the $F_{\rm FB}$ function.

V. CONCLUSIONS

It has been shown that low-frequency ultrasonic attenuation spectra, at various reduced temperatures t between 4.5×10^{-4} and 3.9×10^{-2} measured for the ethanol/dodecane mixture of critical composition, in the dominating part of the reduced frequency Ω can be largely represented by the Ferrell-Bhattacharjee empirical scaling function $F_{\rm FB}(\Omega)$ [1]. To obtain agreement between the experimental data and the theoretical predictions, it is necessary to carefully subtract the background contribution, as measured at frequencies above 100 MHz, from the total attenuation spectra. In addition, suitable crossover corrections have to be applied. For these corrections we performed dynamic light-scattering measurements allowing us to calculate the effective reduced temperatures of the acoustical attenuation spectra as recently proposed by Ferrell and Bhattacharjee [26]. For small Ω values, $F_{\rm FB}(\Omega)$ systematically exceeds the measured data and for $10<\Omega<500$ the $F_{\rm FB}$ function is somewhat smaller. Particularly in this latter reduced frequency range, the recent Folk-Moser scaling function $F_{\rm FM}$ fits the experimental data better.

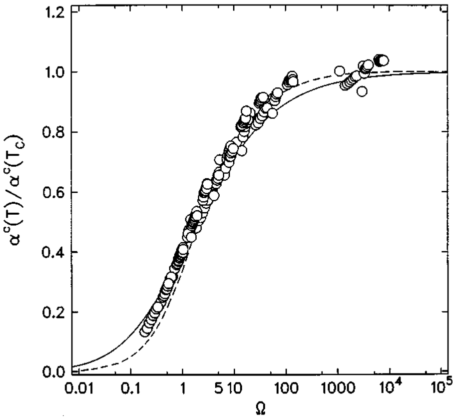

FIG. 6. Lin/log plot of the data from Fig. 5. The full curve again represents the $F_{\rm FB}$ function. The dashed curve is the graph of the Folk-Moser scaling function $F_{\rm FM}$ in the ϵ expansion. The latter has been taken from Fig. 10 of Ref. [31].

The amount of the adiabatic coupling constant derived from the sonic spectra agrees with the value which, on the basis of the two-scale factor universality hypothesis, has been calculated from thermodynamic data. This result supports the idea of universality in the critical dynamics of binary liquids with a miscibility gap.

The half-attenuation frequency $\Omega_{1/2}$ for our system adopts values between 1 and 1.4, at variance with $\Omega_{1/2}$ derived from ultrasonic attenuation data of the literature. As the latter have not been corrected for crossover effects, no clear-cut conclusion can be given on the numerical relationship between the order-parameter relaxation rate and the imposed sound frequency, which has been suggested to also display universality [26].

In conformity with the theoretical predictions by Tanaka and Wada, our low-frequency data (Fig. 3) may be taken to point at a small frequency dependence in the critical amplitude. This suggestion still has to be verified by measurements at even lower frequencies. For such measurements, however, the ethanol/dodecane system is less appropriate, due to its small critical contribution to the sonic attenuation spectra.

ACKNOWLEDGMENTS

We thank Professor P. K. Khabibullaev for sending us his experimental data and Professor R.A. Ferrell for helpful discussions. Financial assistance by the DAAD (Bonn, FRG) and the Volkswagen-Stiftung (Hannover, FRG) is gratefully acknowledged.

[1] R. A. Ferrell and J. K. Bhattacharjee, Phys. Rev. A **31**, 1788 (1985).

[2] B. I. Halperin and P. C. Hohenberg, Phys. Rev. **177**, 952 (1969).

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

[4] H. Tanaka and Y. Wada, Phys. Rev. A **32**, 512 (1985).

[5] M. A. Anisimov, V. P. Voronov, V. M. Malishev, and V. V. Svadkovskii, Éksp. Teor. Fiz., Pis'ma Red. **18**, 224 (1973) [JETP Lett. **18**, 133 (1973)].

[6] C. W. Garland and G. Sanchez, J. Chem. Phys. **79**, 3090 (1983).

[7] H. Dunker, D. Woermann, and J. K. Bhattacharjee, Ber. Bunsenges. Phys. Chem. **87**, 591 (1983).

[8] M. Brai and U. Kaatze, J. Phys. Chem. **96**, 8946 (1992).

[9] U. Kaatze, K. Lautscham, and W. Berger, Chem. Phys. Lett. **144**, 273 (1988).

[10] J. K. Bhattacharjee and R. A. Ferrell, Phys. Rev. A **24**, 1643 (1981).

[11] K. Kawasaki, Ann. Phys. (N.Y.) **61**, 1 (1970).

[12] R. A. Ferrell, Phys. Rev. Lett. **24**, 1969 (1970).

[13] According to FB [see Eq. (4.12a) in Ref. [12]], the singular and the background part of the heat capacity depend on frequency.

[14] E. A. Clerke, J. V. Sengers, R. A. Ferrell, and J. K. Bhattacharjee, Phys. Rev. A **27**, 2140 (1983).

[15] A. W. Francis, Adv. Chem. Ser. **31**, 77 (1961).

[16] K. Orzechowski, J. Chem. Soc., Faraday Trans. **90**, 2757 (1994).

[17] U. Kaatze, B. Wehrmann, and R. Pottel, J. Phys. E **20**, 1025 (1987).

[18] F. Eggers, U. Kaatze, K. H. Richmann, and T. Telgmann, Meas. Sci. Technol. **5**, 1131 (1994).

[19] U. Kaatze, K. Lautscham, and M. Brai, J. Phys. E **21**, 98 (1988).

[20] B. C. Miller, E. A. Clerke, and S. C. Greer, J. Phys. Chem. **87**, 1063 (1983).

[21] J. A. Riddick, W. B. Bunger, and T. K. Sakano, in *Physical Properties and Methods of Purifications. Organic Solvents*, 4th ed., edited by A. Weissberger, E. S. Proskauer (Wiley, New York, 1986).

[22] *Landolt-Börnstein. Physikalisch-Chemische Tabellen*, edited by W. A. Roth and K. Scheel (Springer, Berlin, 1931), Vol. 2.

[23] U. Duerr, S. Mirzaev, and U. Kaatze (unpublished).

[24] L. I. Lisnyanskii and Yu. S. Manucharov, Akust. Zh. **22**, 61 (1976) [Sov. Phys. Acoust. **22**, 33 (1976)].

[25] P. K. Khabibullaev, S. S. Aliev, I. Shakhparonov, and L. E. Kvasova, in *Fizika i Fizika - Khimiya Zhidkostey*, edited by M. I. Shakhparonov (Mosk. Gos. Univ., Moscow, 1972), Vol. 2, p. 94.

[26] J. K. Bhattacharjee and R. A. Ferrell, Physica A **250**, 83 (1998).

[27] R. Dengler and F. Schwabl, Europhys. Lett. **24**, 24 (1993).

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

[29] A. Onuki, J. Phys. Soc. Jpn. **66**, 511 (1997).

[30] R. Folk and G. Moser, Phys. Rev. E **57**, 705 (1998).

[31] R. Folk and G. Moser, Phys. Rev. E **58**, 6246 (1998).

[32] R. Folk and G. Moser, Int. J. Thermophys. **19**, 1003 (1998).