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Dispersion of Ultrasonic Waves in the Binary Mixture Nitrobenzene-*n*-Hexane near a Critical Point

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We report on recent measurements of the ultrasonic velocity in the binary mixture nitrobenzene–*n*-hexane in the homogeneous phase above T_c. The observed dispersion in the range 5–55 MHz has been compared with the prediction of a modified form of the Fixman–Kawasaki theory.

I. INTRODUCTION

The propagation of ultrasonic waves in critical fluids occurs in a different way in one-component and two-component systems.[1] The most striking difference has been known for a long time, and it is observed in the behavior of the ultrasonic velocity. In xenon, CO_2, or helium, the ultrasonic velocity near the critical point is typically of the order of 100 m/sec and decreases on approaching the critical point in a way which is related to the anomalous increase of the heat capacity at constant volume.[1] In contrast, near a critical consolute point of a binary mixture, such as aniline-cyclohexane or nitrobenzene–*n*-hexane, the ultrasonic velocity is typically of the order of 1000 m/sec, and no anomalous behavior is observed on approaching the critical point.[1] Such a fact may be related to the existence of a rigorous thermodynamic bound for the adiabatic compressibility at constant concentration.[2]

Another difference has been recently reported in the high-frequency behavior of the absorption coefficient per wavelength.[3,4] It has been suggested[4] that it might be related to the different behavior of the sound velocity, but further experimental and theoretical investigations are necessary to clarify this point.

Beside these differences certain similarities have been observed. A significant one has been pointed out only very recently.[3,4] In both cases the absorption per wavelength depends on temperature and frequency only through the single reduced variable $\omega^* = \omega/\omega_T$, where $\omega_T = (2\Lambda/\rho C_p)\kappa^2$ for a simple fluid, and $\omega_D = (2\alpha/\rho)(\partial\mu/\partial x)_{Tp}\kappa^2$ for a binary mixture, where ρ is the density, Λ the thermal conductivity, α is the Onsager coefficient for diffusion, C_p is the specific heat at constant pressure, $\mu = \mu_1/m_1 - \mu_2/m_2$ is the Landau chemical potential, $\kappa = \xi^{-1}$ is the inverse correlation length, and x is the concentration.

This possibility of scaling is predicted by the theory proposed by Fixman[5,6] and improved by Kawasaki[7] which we will refer to as the Fixman–Kawasaki (FK) theory. This theory predicts (beside a large increase in the sound absorption) a small, but detectable, dispersion. The effect is bigger in simple fluids than in binary mixtures. Velocity measurements exist for xenon in a large range of frequency and temperature. Cummins and Swinney[8] have recently compared these data with the FK theory. They used the low-frequency form of the theory[7] in the entire frequency range and this may have caused some problem.

The purpose of the present work is to report on recent measurements of the velocity of ultrasound in the mixture nitrobenzene–*n*-hexane at the critical concentration in the homogeneous phase above the critical point.[9] A comparison with the FK theory is also included. The possibility of fitting our data with a single relaxation time has been previously discarded.[10]

A brief outline of the paper is as follows: Sec. II is devoted to an alternative presentation of the FK theory along a line recently proposed by one of us (L. M.),[3,4,11] while in Sec. III the experimental method is described. Section IV contains our experimental results and a comparison with light-scattering data, as well as a comparison with the theory as developed in Sec. II. Finally, the results are summarized and discussed in Sec. V.

II. THEORY

Some time ago, Fixman[5] proposed that a nonlinear coupling between sound waves and concentration fluctuations might explain the anomalous acoustic behavior in the critical region of a binary mixture. There is, by now, good experimental evidence that his relaxation model provides an excellent qualitative explanation of sound propagation in such a system. At the same time, however, it has been realized that many of the additional assumptions introduced to perform the calculation are subject to criticism.[12] The problem of sound propagation near a critical point has recently been reconsidered by Kawasaki[7] in a more general context. Although the physical model proposed by Fixman has been retained by Kawasaki, the calculation has been performed in a different way, and many of the difficulties mentioned above are not present in the Kawasaki formulation. The predictions of this (FK) theory have been compared successfully with sound-absorption data in xenon and in this connection a modified version of the original Fixman theory has been shown to give results identical to those obtained by Kawasaki.[3] Although Kawasaki has explicitly formulated his calculation for the liquid-gas critical point in one-component systems, one can apparently use the correspondence suggested by Swift[13] to translate the result for the liquid-liquid critical point in two-component systems. This is the point of view that we adopted in a previous paper[4] for the sound absorption, and we obtained the following result for the attenuation per wavelength:

$$(\alpha_\lambda)_{\text{crit}} = 2\pi A(T)\omega^* g'(\omega^*) , \tag{1}$$

where

$$A(T) = \frac{k_B T^3}{2\pi^2\rho^3} \frac{1}{c_0^2 C_{V,x}} \left(\frac{\partial p}{\partial T}\right)_{V,x} \kappa \left(\frac{\partial \kappa}{\partial T}\right)^2_{S,x} ,$$

$$g'(\omega^*) = \int_0^\infty dy \frac{y^2}{(1+y^2)^2} \frac{K(y)}{K^2(y)+\omega^{*2}} ,$$

$$K(y) = \tfrac{3}{4}[1+y^2+(y^3-1/y)\tan^{-1}y] ,$$

$$y = q\kappa^{-1} , \quad \omega^* = \omega/\omega_D \quad (\omega_D = 2DK^2) ,$$

where D is the diffusion coefficient,

$$c_0 = (1/\rho\beta_{S,x})^{1/2}$$

is the thermodynamic sound velocity, and $C_{V,x}$ the specific heat at constant volume and concentration. Accordingly, we get for the dispersion for $c(\omega) - c_0/c_0 \ll 1$,

$$c(\omega) - c_0/c_0 = A(T)\omega^{*2} g''(\omega^*) , \tag{2}$$

where

$$g''(\omega^*) = \int_0^\infty dy \frac{y^2}{(1+y^2)^2} \frac{1}{K^2(y)+\omega^{*2}} .$$

The behavior of the thermodynamic coefficient $A(T)$ can be estimated with the help of a recent work by Griffiths and Wheeler.[14] According to these authors, $C_{V,x}$ should remain finite at the critical point unless the critical temperature is a maximum or a minimum in the $T_c = T_c(x_c)$ curve; c_0 should not be zero unless the critical pressure is an extremum in the $p_c = p_c(x_c)$ curve; and finally, $(\partial p/\partial T)_{V,x}$ should become equal to $(\partial p/\partial T)_{\text{crit}}$ along the critical line. As a consequence, excluding the two particular cases, and assuming $\kappa \propto (\Delta T)^\nu$, one gets $A(T) \propto (\Delta T)^{3\nu-2}$ or, using the scaling relation $\alpha = 2 - 3\nu$, $A(T) \propto (\Delta T)^{-\alpha}$. In contrast, for a simple fluid, we get $A(T) \propto (\Delta T)^{\alpha+3\nu-2} \propto (\Delta T)^\circ$. Our measurements[4,12,15] of the sound-absorption coefficient in aniline-cyclohexane and nitrobenzene–n-hexane are not in disagreement with an increasing $A(T)$ as $\Delta T \to 0$, but it should be pointed out that in this case both at low and high frequencies the behavior of α_λ is essentially determined by the integral in Eq. (1).

The situation is different as far as dispersion is concerned. In this case for low frequencies $c(\omega)$ reduces to c_0, while for high frequencies according to Eq. (2) it approaches the value $c_0[1+\frac{1}{4}\pi A(T)]$ and therefore should increase without limit as the critical point is approached. This conclusion suggests that the theory in its present form cannot be used to describe sound propagation very close to T_c or alternatively at high frequency. In a previous paper[12] the same conclusion was reached observing that for high values of ω^* the main contribution to the integral appearing in Eqs. (1) and (2) arises from high values of y and in this region the Ornstein–Zernike form of the correlation function is not expected to be valid. However, looking at the original derivation[5] of Eqs. (1) and (2), we find a possible origin for the unphysical result. A basic assumption in Fixman's derivation is that $C_{p,x}$ and $C_{V,x}$ receive the same increment from the composition fluctuations. Now, after the proof of the existence of a thermodynamic bound for $C_{V,x}$,[2] such an assumption is no longer justified. A modified version of Fixman's theory which avoids this difficulty can be formulated as follows.[11] The best thing to do in order to avoid thermodynamic inconsistency is to construct the objects of the theory according to thermodynamic rules. This procedure is obviously not satisfactory from the microscopic point of view. However, it has the advantage of being very simple and, moreover, it often happens to be a guide for a more fundamental approach.

In the one-component case a frequency-dependent heat capacity was derived following the scheme outlined in Table I. A frequency-dependent specific heat for the binary mixture case has been constructed according to this scheme using the thermodynamic analogy suggested by Rowlinson.[16] Accordingly, the quantity which in a binary mixture corresponds to the free energy $F = U - TS$ is the Gibbs function $G = H - TS$, where H is the enthalpy, expressed as a function of temperature

TABLE I. Comparison of one- and two-component systems.

One-component systems	Two-component systems
$\delta F=\frac{1}{2V}\sum_{q<q_{\max}} a(q)\lvert\rho(q)\rvert^2$	$\delta G=(1/2V)\sum_{q<q_{\max}} a_M(q)\lvert x(q)\rvert^2$
free energy associated with long-wavelength density fluctuations;	Gibbs function associated with long-wavelength concentration fluctuations;
$\langle\lvert\rho(q)\rvert^2\rangle=K_BTV/a(q)$	$\langle\lvert x(q)\rvert^2\rangle=K_BTV/a_M(q)$
mean-square density fluctuations according to thermodynamic fluctuation theory;	mean-square concentration fluctuations according to thermodynamic fluctuation theory;
$\langle\lvert\rho(q)\rvert^2\rangle=A(q^2+\kappa^2)^{-1+\eta/2}$	$\langle\lvert x(q)\rvert^2\rangle=A_M(q^2+\kappa_M^2)^{-1+\eta/2}$
Ornstein–Zernike form as modified by the small Fisher correction, presumably valid for $y=q\kappa^{-1}\lesssim 1$;	Ornstein–Zernike form as modified by the small Fisher correction, presumably valid for $y=q\kappa_M^{-1}\lesssim 1$;
$\delta U=-T^2\frac{\partial}{\partial T}\left(\frac{\partial F}{T}\right)_{V,N}=-\frac{T}{2V}\sum_{q<q_{\max}}\frac{\partial a(q)}{\partial T}\lvert\rho(q)\rvert^2$	$\delta H=-T^2\frac{\partial}{\partial T}\left(\frac{\delta G}{T}\right)_{p,x}=-\frac{T}{2V}\sum_{q<q_{\max}}\frac{\partial a_M(q)}{\partial T}\lvert x(q)\rvert^2$
internal energy associated with long-wavelength density fluctuations;	enthalpy associated with long-wavelength concentration fluctuations;
$C'_V=\frac{1}{K_BT^2\rho V}\langle(\delta U)^2\rangle_c$	$C'_{p,x}=\frac{1}{K_BT^2\rho V}\langle(\delta H)^2\rangle_p$
specific heat associated with long-wavelength density fluctuations, the average is taken in a canonical ensemble;	specific heat associated with long-wavelength concentration fluctuations, the average is taken in an isothermal isobaric ensemble;
$\tilde{C}_V(\omega)=C_V+\frac{i\omega}{K_BT^2\rho V}\int_0^\infty dt\, e^{i\omega t}\langle\delta V(0)\delta U(t)\rangle_c$	$\tilde{C}_{p,x}(\omega)=C_{p,x}+\frac{i\omega}{K_BT^2\rho V}\int_0^\infty dt\, e^{i\omega t}\langle\delta H(0)\delta H(t)\rangle_p$
$\equiv C_V+\Delta(\omega),\quad \Delta(\omega)=\Delta'(\omega)+\Delta''(\omega)$	$\equiv C_{p,x}+\Delta_M(\omega),\quad \Delta_M(\omega)=\Delta'_M(\omega)+\Delta''_M(\omega)$
complex frequency-dependent specific heat, note that $\tilde{C}_V(0)=C_V$;	complex frequency-dependent specific heat, note that $\tilde{C}_{p,x}(0)=C_{p,x}$;
$\dot{\rho}(q,t)=-\tau^{-1}(q)\rho(q,t)$	$\dot{x}(q,t)=-\tau_M^{-1}(q)x(q,t)$
time decay of density fluctuations,	time decay of concentration fluctuations,
$\tau^{-1}(q)\rightarrow(\Lambda/\rho C_p)q^2$	$\tau_M^{-1}(q)\rightarrow\frac{\alpha}{\rho}\left(\frac{\partial\mu}{\partial x}\right)_{T,p}q^2$
in the hydrodynamic limit, where Λ is the thermal conductivity;	in the hydrodynamic limit, and $\frac{\alpha}{\rho}\left(\frac{\partial\mu}{\partial x}\right)_{T,p}\equiv D$ is the diffusion coefficient;
$\tau^{-1}(q)=\frac{1}{2}\omega_T K(y)$,	$\tau_M^{-1}(q)=\frac{1}{2}\omega_D K(y)$,
$K(y)$ satisfies both hydrodynamic and dynamic scaling requirements, $\omega_T\equiv(2\Lambda/\rho C_p)\kappa^2$ is the characteristic frequency for sound propagation;	$K(y)$ satisfies both hydrodynamic and dynamic scaling requirements, $\omega_D\equiv 2D\kappa^2$ is the characteristic frequency for sound propagation;
$\Delta(\omega)=\frac{iK_BT^2}{\pi^2\rho}\left(1-\frac{\eta}{2}\right)\kappa\left(\frac{\partial\kappa}{\partial T}\right)^2\int_0^\infty dy\frac{y^2}{(1+y^2)^2}\frac{\omega^*}{K(y)-i\omega^*}$,	$\Delta_M(\omega)=\frac{iK_BT^2}{\pi^2\rho}\left(1-\frac{\eta}{2}\right)\kappa\left(\frac{\partial\kappa}{\partial T}\right)^2\int_0^\infty dy\frac{y^2}{(1+y^2)^2}\frac{\omega^*}{K(y)-i\omega^*}$,
where $\omega^*=\omega/\omega_T$, to derive this expression the Gaussian character of the fluctuations was taken into account;	where $\omega^*=\omega/\omega_D$, to derive this expression the Gaussian character of the fluctuations was taken into account;
$c^2=\frac{1}{\rho\beta_T}\frac{C_p}{C_V}$,	$c^2=\frac{T}{\rho^2}\left(\frac{\partial p}{\partial T}\right)_{\rho,x}\frac{C_{p,x}}{C_{V,x}(C_{p,x}-C_{V,x})}$,
$\tilde{c}^2(\omega)=\frac{1}{\rho\beta_T}\frac{C_p+\Delta(\omega)}{C_V+\Delta(\omega)}$;	$\tilde{c}^2(\omega)=c^2\frac{1+\Delta_M(\omega)/C_{p,x}}{1+\Delta_M(\omega)/C_{p,x}-C_{V,x}}$;
$\left.\begin{aligned}\alpha_\lambda(\omega)&=\pi\frac{\gamma-1}{C_p}\Delta''(\omega),\\ \frac{c(\omega)-c}{c}&=-\frac{\gamma-1}{2C_p}\Delta'(\omega)\end{aligned}\right\}\left(\gamma=\frac{C_p}{C_V}\right)$	$\left.\begin{aligned}\alpha_\lambda(\omega)&=\pi\frac{1}{C_{p,x}(\gamma_M-1)}\Delta''_M(\omega),\\ \frac{c(\omega)-c}{c}&=-\frac{1}{2C_{p,x}(\gamma_M-1)}\Delta'_M(\omega)\end{aligned}\right\}\left(\gamma_M=\frac{C_{p,x}}{C_{V,x}}\right)$

and concentration at constant pressure. The salient features of this procedures are compared in Table I with the analogous steps in the one-component case. A complex frequency-dependent sound velocity $\tilde{c}(\omega)$ is then obtained by means of standard thermodynamic relations. The procedure is outlined in the last few lines of Table I.

As we shall see in Sec. IV our experimental results cannot be used to discriminate between the present calculation and a straightforward transcription for binary mixtures of the Kawasaki theory. Indeed, as far as the theories are concerned, the only difference between the two approaches is in the thermodynamic factor $A(T)$ determining the magnitude of the effect (dispersion or sound absorption). This factor could be calculated from heat capacities data, but as far as we know, these data are not available for our system.

III. EXPERIMENTAL

A. Materials

The nitrobenzene–n-hexane system, according to the solubility curve given by Timmermans,[17] has an upper critical temperature of $T_c = 21.0$ °C at the critical concentration of 51.7 wt% of $C_6H_5NO_2$, i.e., of $x_c = 0.428$ mole fraction nitrobenzene. In the same system but with a noncontrolled purity of the two components D'Arrigo and Sette[15] found a flat maximum at 21.0 °C around a concentration of 0.37 mole fraction $C_6H_2NO_2$. A more recent experimental determination of the coexistence curve by Chen and Polonsky[18] gives $T_c = (20.20 \pm 0.10)$ °C at $x_c = 0.42$. Finally Aliev and Khabibullaev[19] report $T_c = 20.98$ °C and $x_c = 0.401$. In the present experiment the sample was prepared from RS-grade n-hexane (spectrophotometric grade, purity 99.9%) and RP-grade nitrobenzene (purity 99.0%) both from the Carlo Erba Co. Each component was distilled under a pressure of about 6 cm Hg in order to eliminate benzene. Hexane was doubly distilled in a cromatography column with silica gel. Nitrobenzene was doubly distilled in presence of $CaCl_2$. A critical mixture of $x_C = 0.428$, prepared with these components, has a critical temperature between 19.597 (two homogeneous phases) and 19.691 °C (one homogeneous phase). The appearance of the meniscus was observed, after prolonged thermal stabilization, by means of the particular behavior of the ultrasonic signals and further controlled with velocity measurements, as will be explained later. The difference between our observed critical temperature and those reported in Refs. 15 and 17–19 may be due, beside the eventual presence of impurities, to the following causes: (i) The sample was heated at a temperature of about 30 °C and then poured into the ultrasonic cell. (ii) The necessity of a free volume above the mixture of the order of the volume occupied by the liquid itself was imposed by the experimental method, where the path length of the ultrasounds must be varied. In both cases there could be a concentration variation of the mixture which causes phase separation to occur at a lower temperature.

B. Experimental Procedure

Absolute velocity measurements were made by a standard phase comparison technique.[20] Electrical pulses, obtained by a gating process by means of a slightly modified Arenberg pulsed oscillator (PG-650C) from a continuous wave signal generator (HP-606B), excite the transmitting transducer. The received acoustic signal is amplified and mixed with a continuous coherent reference signal from the cw generator. In this way, maxima and minima in the resulting electrical pulse amplitude occur as the path length of ultrasounds is varied, thus giving a measure of the wavelength. Path lengths are measured by means of an accurate micrometer (sensitivity up to 5×10^{-4} mm) and the frequency is measured with an electronic counter.

Great care was employed in the temperature stabilization: we used a Leeds and Northrup model No. 8401 constant-temperature bath which provides uniform and stable control within 0.001 °C over a large volume for long periods. The temperature was measured by means of a platinum resistance thermometer; the error in this determination was less than 0.005 °C.

In order to test the temperature stabilization inside the ultrasonic cell, a thermocouple was used to indicate the difference between the temperature of the sample and the thermostatic fluid. Measurements were made only after a long stabilization time (about 12 h), when the thermocouple showed no appreciable temperature difference. The velocity of ultrasounds was measured as a function of the frequency between 5 and 55 MHz (5, 15, 25, 35, 45, and 55 MHz) at ten different temperatures ranging from 19.972 to 21.131 °C.

The experimental results are reported later in Table II. The error in the experimental determination was estimated to be not greater than ±0.5 m/sec by means of a careful study of the repeatability of the single measurement. At this end it is worthwhile noting that, in order to check the experimental setup, a large number of measurements were carried out in pure liquids (as n-hexane and benzene) where there is no relaxation in the frequency range examined and indeed no dispersion was observed within the previously quoted experimental error. Another check was made during the actual measurement by testing the

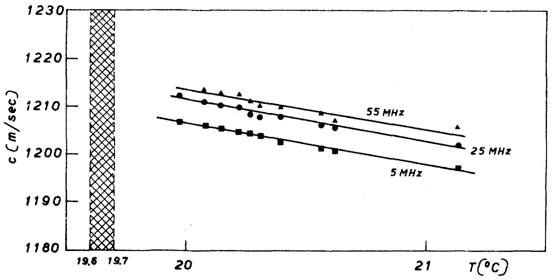

FIG. 1. Sound velocity vs temperature for some ultrasonic frequencies ($x_0 = 0.428$ molar fraction of nitrobenzene; $19.597\,°C < T_c < 19.691\,°C$).

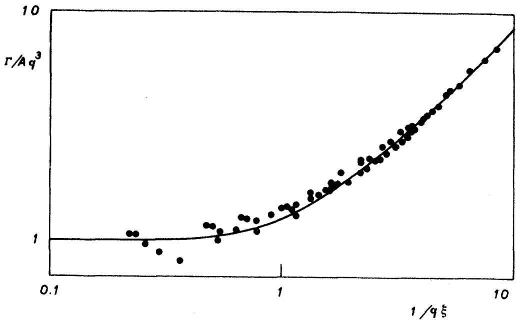

FIG. 2. $\Gamma(q)/Aq^3$ vs $1/T$ (Kawasaki plot). The data are those reported by Chen and Polonsky (Ref. 18).

repeatability of the experimental points. In order to verify if our results were essentially due to critical effects, we have performed a further set of measurements far from the critical point, namely, at a temperature of 29.862 °C. We obtained $c = 1180.83$, 1180.82, and 1180.40 m/sec, respectively, at 5, 15, and 25 MHz. These results show no dispersion.

IV. EXPERIMENTAL RESULTS AND COMPARISON WITH THEORY

Sound velocity data obtained as described in Sec. III are collected in Table II. Measurements made away from the critical point at the temperature of 29.862 °C clearly indicate no dispersion, while for measurements made close to the critical point, for example, at $T = 20.079\,°C$, we find a dispersion of ~0.6% in the range of frequency investigated. In Fig. 1 the temperature dependence of the sound velocity is reported. In contrast to what is observed near the critical point of simple fluids, no anomaly is observed. This behavior is in agreement with the existence of a thermodynamic bound for $\beta_{S,x}$.

A comparison of our experimental results with the theory presented in Sec. II requires information which cannot be obtained from our measurements. In fact, as it stands, the theoretical prediction consists of a family of curves depending on a number of parameters such as the critical temperature, the diffusion coefficient, the correlation length, heat capacities, etc. These parameters can be determined, to a degree by means of independent measurements. Some information can be derived from our previous sound absorption measurements, while more precise information can be obtained about the diffusion coefficient and the correlation length from light scattering experiments. For this reason, measurements of the Rayleigh linewidth $\Gamma(q)$ reported by Chen and Polonsky[18] have been analyzed according to the prediction of the Kawasaki theory.

The Kawasaki theory predicts

$$\Gamma(q) = D\kappa^2 K(y) , \tag{3}$$

where $\Gamma(q)$ is the decay constant for concentration fluctuations and D is the diffusion coefficient. Assuming $D = D_0\epsilon^{\nu}$, $\xi = \xi_0\epsilon^{-\nu}$ [where $\epsilon = (T - T_c)/T_c$] and putting $A = D_0\xi_0$, Eq. (3) can be written as

$$\Gamma(q)/Aq^3 = K(y)/y^3 . \tag{4}$$

TABLE II. Sound-velocity data in nitrobenzene–n-hexane, $T_c = 19.597\,°C$, $x_c = 0.428$ molar fraction of nitrobenzene.

f (MHz) T (°C)	5	15	25	35	45	55
29.862	1180.83	1180.82	1180.40	...	...	...
21.131	1197.43	1201.95	1203.75	1204.25	1205.03	1205.67
20.619	1200.04	1204.01	1205.28	1206.58	1206.91	1207.00
20.559	1201.19	1204.43	1206.10	1207.72	1208.08	1208.49
20.391	1202.40	1205.88	1207.53	1208.15	1209.43	1209.60
20.305	1203.01	1206.15	1207.59	1208.85	1209.87	1209.89
20.266	1204.04	1207.50	1208.25	1209.27	1210.42	1211.02
20.221	1204.64	1207.90	1209.72	1210.54	1211.80	1212.52
20.143	1205.34	1208.97	1209.87	1211.81	1212.44	1212.70
20.079	1205.90	1210.39	1210.89	1212.30	1213.18	1213.40
19.972	1206.89	1210.75	1212.28	1213.30	...	...

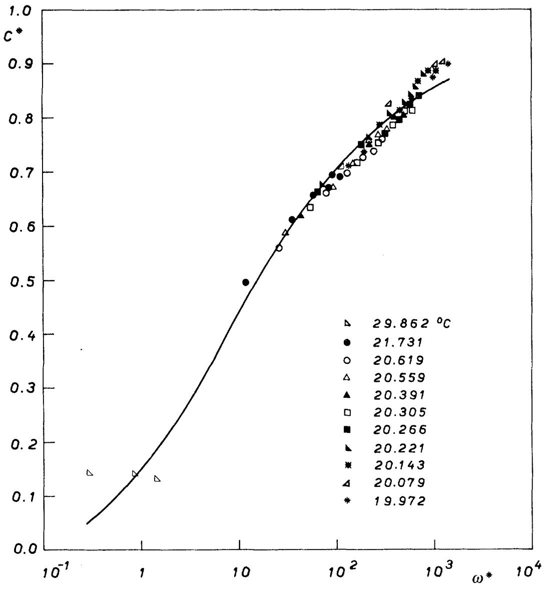

FIG. 3. Reduced velocity c^* vs ω^*.

The fitting of Eq. (4) (which is usually called the Kawasaki plot) with experimental results is shown in Fig. 2. For the quantities D_0, ξ_0, ν, and T_c, which are the parameters to be obtained from the fit, we get the values $\nu = 0.67$, $\xi_0 = 2.03$ Å, $D_0 = 1.65\times10^{-5}$ cm^{2}sec^{-1}, and $T_c = 20.20$ °C. It is then possible to obtain the characteristic frequency $\omega_D = 2D\kappa^2 = \omega_0\epsilon^{3\nu}$, where $\omega_0 = 2D_0/\xi_0^2 = 8.01\times10^{10}$ sec^{-1}. If we compare this value with that obtained in the previous independent fit of sound-absorption data,[4] we find good agreement. For example, at $T = 24.3$ °C ($T_c = 21$ °C), we found $f_D = \omega_D/2\pi = 1.52\times10^6$ sec^{-1} and with $3\nu = 2$ it results $\omega_0 = 7.54\times10^{10}$ sec^{-1}. Moreover we can calculate the shear viscosity $\eta_{\text{theor}} = k_B T/6\pi D\xi$ and compare it with the values (η_{expt}) measured by Drapier.[21] For example, at $T = 21.6$ °C we get $\eta_{\text{theor}} = 6.45\times10^{-3}$ P, while $\eta_{\text{expt}} = 6.51\times10^{-3}$ P.

The information obtained from the Kawasaki plot has been used to fit our velocity data to the prediction of the FK theory as modified in Sec. II. For this purpose the expression used for the sound velocity is

$$c(\omega,\ T) = c(0,\ T)[1 + A(T)\omega^{*2}\mathcal{g}''(\omega^*)]\,, \tag{5}$$

with $c(0,\ T) = c_0 + c_1\epsilon$ and $A(T) = A_0\epsilon^\alpha$, where T_c, ν, A_0, α, c_0, and c_1 are the parameters to be obtained from the fit, while ω_0 has been fixed to the values obtained from the Kawasaki plot. For the free parameters we found the values

$$T_c = 19.60\,^\circ\mathrm{C}\,,\quad \nu = 0.65\,,\quad A_0 = 0.043\,,\quad \alpha = 0.006\,;$$

$$c_0 = 1179\ \mathrm{m/sec}\,,\quad c_1 = -100.3\ \mathrm{m/sec}\,.$$

The results are reported in Fig. 3 where the quantity

$$c^* = \frac{c(\omega,\ T) - c(0,\ T)}{c(\infty,\ T) - c(0,\ T)}$$

is plotted versus ω^*.

V. CONCLUSIONS

We have measured the sound velocity in the critical mixture nitrobenzene–n-hexane as a function of temperature and frequency in the homogeneous phase above T_c. At fixed frequency, the sound velocity is a linear function of temperature approaching a finite nonzero critical value in agreement with the expected behavior of the adiabatic compressibility at constant concentration[14] to which the sound velocity is related by the equation $c^2 = (\rho\beta_{s,x})^{-1}$. At fixed temperature the sound velocity depends on frequency. The observed dispersion has been compared with the prediction of the FK theory as modified in Ref. 11. We find that the theory can be used to describe the observed behavior, in a way which is consistent both with our previous absorption data,[4] the Rayleigh linewidth measurements of Chen and Polonsky[18] as well as independent viscosity measurements.[21] We think, however, that these tests are far from being conclusive. The theoretical prediction strongly depends on a number of parameters, like $c(0,\ T) = c_0 + c_1\epsilon$ and $A(T) = A_0\epsilon^\alpha$, which we have not compared with independent measurements.

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Viscosity and Light Scattering in Critical Mixtures

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Simultaneous measurements of both viscosity and light scattering are performed on two critical mixtures. The first one is a triethylamine-water solution, which exhibits a lower consolute point, the second one a methanol-ciclohexane mixture with an upper consolute point. It is found that the singular behavior of viscosity cannot be fitted by a simple power law, nor by a logarithmic one, in the entire range of temperature. The asymptotic behavior, however, tends to become logarithmic as the critical temperature is approached. The simultaneous observation of scattered light allows one to exclude the intervention of spurious processes, like a breaking of correlations because of impurities. In addition, it is shown that the correlation length seems to depend mainly on the reduced temperature, irrespective of the system under examination.

I. INTRODUCTION

In the present paper we report a series of measurements of viscosity and light scattering, performed simultaneously on a critical binary mixture. There are, in the literature, many measurements on viscosity, the majority of which seem to indicate that, near the critical point, this physical property can exhibit, at most, a logarithmic divergence.[1] However, certain results seem to indicate a stronger divergence, at least at those temperatures not too close to the critical temperature.[2] Now Kawasaki[3] has recently shown that a logical inconsistency would derive from a divergence of viscosity stronger than a logarithmic one, as a consequence of the application of the scaling laws in the frame of the mode-mode coupling theory. Therefore, a divergence in the viscosity stronger than a logarithmic one would indicate that the scaling laws do not apply in that range. As suggested by Tsai,[4] one can postulate the existence of two critical regions. The first one, classical in character, takes place relatively far from the critical point. In such a region the viscosity can diverge strongly. Close to the critical point, however, there is a second critical region, in which scaling laws would apply, and therefore the viscosity can diverge at most logarithmically.

Alternatively, Barber and Champion[2] suggest that impurities of various kinds present in the system prevent the correlation length from becoming larger and larger as the critical point is approached. In such a case the strong divergence of viscosity, observed relatively far from the critical point, would be the effective behavior, while the weak divergence observed near the critical point is simply due to the impurity effect of breaking the critical correlations.

The experiments we report in the present paper are performed in order to discriminate between the two points of view sketched above. For this purpose we perform, on the same sample and at the same time, measurements of both the viscosity and the scattered-light intensity.

We use a vibrating-wire viscometer which allows a good thermostatation by immersing the viscome-