CRITICAL PROPERTIES OF ACOUSTIC WAVE ABSORPTION IN THE BENZONITRILE-ISOOCTANE SYSTEM

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Experimental results for the absorption of ultrasonic waves in critical benzonitrile+isooctane mixtures in the frequency range 5—21 MHz and at temperatures $0.15 \leqslant T - T_c \leqslant 20$ K are reported and confronted with the Shiwa-Kawasaki's mode-coupling theory. The theoretical scaling function was found to describe the experimental results correctly throughout the reduced frequency range $\omega^* < 50$. The values of certain thermodynamic parameters necessary for the determination of the reduced amplitude $A(\varepsilon)$ were calculated using the linear relation between α_c/f^2 and $f^{-1.06}$ predicted by the Bhattacharjee—Ferell dynamic scaling theory.

1. Introduction

Acoustic investigations of critical mixtures are a source of valuable information concerning the dynamical properties of phase transitions [1 — 6]. In the first place, such systems exhibit a strong increase in acoustic wave absorption as they approach the critical point. This anomaly is attributed to the coupling between acoustic field and fluctuations in concentration [9]. Three theoretical models have been proposed for the description of the acoustic wave propagation in critical mixtures: the renormalization group theory [7], the dynamic scaling theory [8], and the mode-coupling theory [9 — 12]. The last one, in the three versions due respectively to KAWASAKI [9], MISTURA [10] and CHABAN [11], after initial success, came up against serious difficulties, in particular the expressions for the critical amplitude failed to describe the experimental data correctly. A drawback of the mode-coupling theory resided in the fact that it led to a scaling function that broke down at high reduced frequencies $\omega^* = \omega/\omega_D$ (where ω_D is a characteristic frequency of fluctuations of the order parameter). Recently several papers have been published aimed at the overcoming of these difficulties. A general expression for the critical amplitude was proposed [13, 14] that comprises the formulae of Kawasaki, Mistura and Chaban as special cases. Moreover, applying the four heat-mode approximation, a new expression for the scaling function was derived [12].

2. Theoretical background

Absorption of acoustic waves in critical mixtures is best represented in the form of the absorption coefficient per wavelength versus the reduced frequency

$$\omega^* = \omega/\omega_D, \tag{2.1}$$

where ω_D denotes the characteristic frequency of fluctuations in concentration. Since the characteristic frequency is a function of temperature, the description in terms of ω^* enables us to comprise in a single graph the results obtained under different experimental conditions of temperature and frequency. For critical mixtures, ω_D takes the form [3]

$$\omega_D = \frac{k_B T_c}{3\pi\eta_s \xi^3} = \frac{k_B T_c}{3\pi\eta_0 \xi_0^3} \, \epsilon^{(3+x_\eta)\nu} = \omega_0 \epsilon^{z\nu}, \tag{2.2}$$

where k_B is the Boltzmann constant and $\epsilon = (T - T_c)/T_c$ the reduced temperature, providing a measure of the distance of the system from the critical point on the temperature scale. The correlation length ξ and shear viscosity η_s occurring in Eq. (2.2) fulfil the following exponential relations near the critical point: $\xi = \xi_0 \epsilon^{-\nu}$ and $\eta_s = \eta_0 \epsilon^{-x_\eta}$. The quantities $z = (3 + x_\eta) = 3.06$ and $\nu = 0.638$ are the so-called critical exponents.

The dynamic scaling hypothesis predicts the anomalous part of the acoustic wave absorption to be a function of the reduced frequency given by the following general expression:

$$\alpha_\lambda = \pi A(\epsilon) I(\omega^*), \tag{2.3}$$

where $A(\epsilon)$ is the critical amplitude and $I(\omega^*)$ the scaling function. Each version of the mode-coupling theory has its own expression for $A(\epsilon)$ [9–11]. However, none of them describes the experimental results satisfactorily. Lately, TANAKA et al. [13] as well as the present authors [14] have re-analyzed this aspect of the theory and obtained the following general formula for $A(\epsilon)$:

$$A(\epsilon) = \frac{k_B g^2 u^2 v^2}{\pi^2 \rho T_c c_p^2 \xi_0^3} \, \epsilon^{-\bar{\alpha}}, \tag{2.4}$$

which for particular cases reduced to the expressions of the different versions of the mode-coupling theory. In (2.4), ρ is the density of the mixture, u the velocity of the ultrasonic wave, c_p the specific heat at constant pressure, and $\bar{\alpha} = 0.11$ the critical exponent for the specific heat. The dimensionless constant g introduced by Bhattacharjee and Ferrel in their dynamic scaling theory has been shown [2] to remain unchanged as the system approaches the critical point. Once the values of all the thermodynamic parameters of the mixture are available, the constant g can be determined from the following formula derived by Tanaka:

$$g = -T_c \alpha_{Pb} + \frac{T_c \alpha_{Pc}}{c_{Pc}} c_{Pb},$$ (2.5)

whre, α_p the thermal expansion coefficient α_p and the specific heat can be expressed by the following exponential relations: $\alpha_P = \alpha_{Pc} \epsilon^{-\tilde{a}} + \alpha_{Pb}$, $c_P = c_{Pc} \epsilon^{-\tilde{a}} + c_{Pb}$. The quantities with the subscript b denote the regular part (showing no critical anomaly) whereas those with subscript c denote the amplitude of the critical part. The critical amplitude $A(\epsilon)$ given by Eq. (2.4) is a function only of the reduced temperature ϵ. However as shown by TANAKA et al. [13], it should depend also on the frequency ω. This circumstance, resulting from the frequency-dependence of the specific heat, results in the breakdown of the dynamic scaling hypothesis for the acoustical anomaly. Since this dependence is noticeable only at very high values of the reduced frequency, it can be neglected in the usually accessible range of frequencies.

The expression (2.3) states that all the values of the absorption coefficients (all the α's measured for different temperatures and frequencies and divided by the critical amplitude) scale along the single universal curve $I(\omega^*)$, referred to as the scaling function. This function depends on but one variable — the reduced frequency. Earlier versions of the mode-coupling theory applied a perturbation procedure taking into account only two heat-mode intermediate states. According to these approximations, the scaling function has the form [9]:

$$I^{(2)}(\omega^*) = \int_0^\infty dx \, [xy(x)]^2 \, \frac{\omega^* K(x)}{K^2(x) + \omega^{*2}},$$ (2.6)

where x is the product of the wave number k and the correlation length ξ. The function $y(x)$, defined as the derivative of the logarithm of the correlation function of the order parameter $X(x)$ takes the form:

$$y(x) = 1 - \frac{\eta}{2} + x \, \frac{d}{dx} \ln X(x),$$ (2.7)

where $\eta = 0.041$ is the critical exponent introduced by FISHER [15]. The function $K(x)$ is defined in terms of the decay rate of fluctuations of the wave number k. The explicit form of $K(x)$, as proposed by KAWASAKI [8], is

$$K(x) = \frac{3}{4} [1 + x^2 + (x^3 - 1/x) \arctan(x)].$$ (2.8)

The scaling function in the two heat-mode approximation has been shown to be inadequate for the description of the experimental results, particularly for high reduced frequencies [16]. This led SHIWA and KAWASAKI [17] to extend a perturbation procedure to include the contributions of four heat-mode intermediate states to the bulk viscosity. They obtained the scaling function in the form of the sum $I^{(2)}(\omega^*) + I^{(4)}(\omega^*)$, with $I^{(4)}(\omega^*)$ given by

$$I^{(4)}(\omega^*) = \frac{1.42^2}{54\pi^3} \int\limits_0^\infty dx_1 \int\limits_0^\infty dx_2 \int\limits_0^\infty dx_3 \int\limits_0^\pi d\theta_2 \int\limits_0^\pi d\theta_3 \int\limits_0^{2\pi} d\phi \times$$

$$\times (x_1 x_2 x_3)^2 \cdot \sin\theta_2 \sin\theta_3 \cdot \omega^* \Re(x_1, x_2, x_3, \theta_2, \theta_3, \phi). \tag{2.9}$$

The explicit form of $\Re(x_1, x_2, x_3, \theta_2, \theta_3, \phi)$ is to be found in ref. [17].

The key to the successful use of the mode-coupling theory resides in a proper choice of the correlation function of the order parameter fluctuations occurring in the formulae (2.8) and (2.9), since the expression for $I(\omega^*)$ is highly sensitive to the form of the correlation function $X(x)$ for high values of x, i.e. when ω^* is large. Earlier versions of the mode-coupling theory applied the Ornstein – Zernike formula [17]. However, the latter is well known to fail to account correctly for the long-range "tail". Thus the $X(x)$ for $x \gg 1$ has to be replaced by the Fisher-Langer expression [18]. Recently, BRAY [19] proposed an approximation of the correlation function ideally reproducing the shape of the Ornstein-Zernike and Fisher-Langer functions for small and large values of x, respectively.
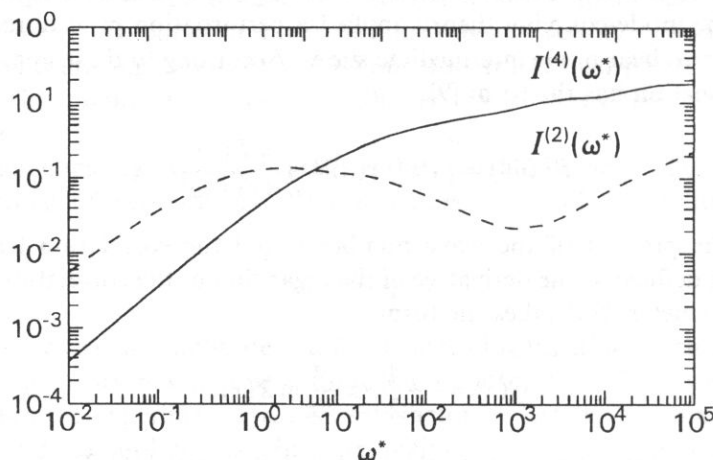

Fig. 1. $I^{(2)}(\omega^*)$ (dashed) line and $I^{(4)}(\omega^*)$ (solid line) calculated from the Bray's function.

The numerically determined values of $I^{(2)}(\omega^*)$ (dashed line) and $I^{(4)}(\omega^*)$ (solid line) are plotted in Fig. 1. In both cases, Bray's expression has been used for the correlation function.

With regard to the nature of the initial kinetic equations involved, the mode-coupling theory is unable to describe the absorption and dispersion of ultrasonic waves *versus* frequency at the critical point as such (the "critical region"). Ferrell and Bhattacharjee succeeded in deriving an expression of this kind that is owing to their highly ingenious use of the dynamic scaling hypothesis. They postulate that at the critical point the absorption coefficient α_c/f^2 should depend linearly on $f^{-1.06}$:

$$\frac{\alpha_c}{f^2} = \left[\frac{\pi^2 \bar{\alpha} g^2 u_c c_{Pc}}{2zvT_c c_{Pb}^2} \left(\frac{\omega_0}{2\pi} \right)^{\bar{\alpha}/zv} \right] f^{-(1+\bar{\alpha}/zv)} + \frac{\alpha^b}{f^2} = S f^{-1.06} + b,$$
(2.10)

with α^b/f^2 — classical absorption. Eq. (2.10) has been confirmed repeatedly by experiment [3−6]; it has proved to be a highly useful tool permitting the determination of the coupling constant g. Whereas the counterpart of Eq. (2.3) in the dynamic scaling theory is given by the expression

$$\alpha_\lambda = \pi \frac{\pi \bar{\alpha} u^2 g^2 c_{Pc} \epsilon^{-\bar{\alpha}}}{2zvT_c c_{Pb}^2} \frac{(\omega^*)^{-\bar{\alpha}/zv}}{[1+(\omega^*)^{-1/2}]^2} = \pi A_{FB}(\epsilon) G(\omega^*).$$
(2.11)

3. Experimental results

The measurements were carried out by the pulse-echo method using an experimental set-up developed by MATEC. The details of the measuring position as well as the evaluation of the accuracy achieved are given elsewhere [20, 21]. The critical mixture of benzonitrile + isooctane (2,2,4-trimethylpentane) exhibits an upper critical point, and the critical parameters of the separation curve are [22]: $T_c = 18.71°C$ and $x_c = 0.465$ (molar fraction of benzonitrile). Our measurements of the ultrasound velocity and absorption covered the temperature range $\Delta T = T - T_c = 0.1$ K to 20.2 K for five frequencies of the ultrasonic wave: 5, 7, 10, 15 and 21 MHz.

The measurement started at 40°C and the temperature was then lowered gradually down to the critical one. The velocity of the ultrasound as function of temperature was found to be linear: $u = 1205 - 3.5 (T - T_c)$. To within the experimental error, no dispersion of the velocity was found throughout the frequency limits ranging from 5 to 25 MHz. Figure 2 shows the velocity as a function of temperature.
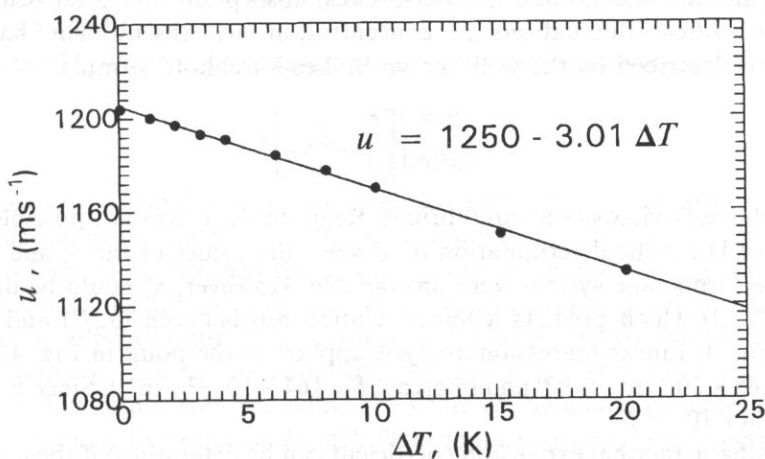

Fig. 2. Propagation velocity of ultrasonic waves versus ΔT in the critical benzonitrile + isooctane system.

In Fig. 3, the absorption per wavelength is plotted as a function of temperature. The graph is typical for critical mixtures: the absorption grows progressively as the system approaches the critical temperature, the quicker the lower is the frequency of the wave.
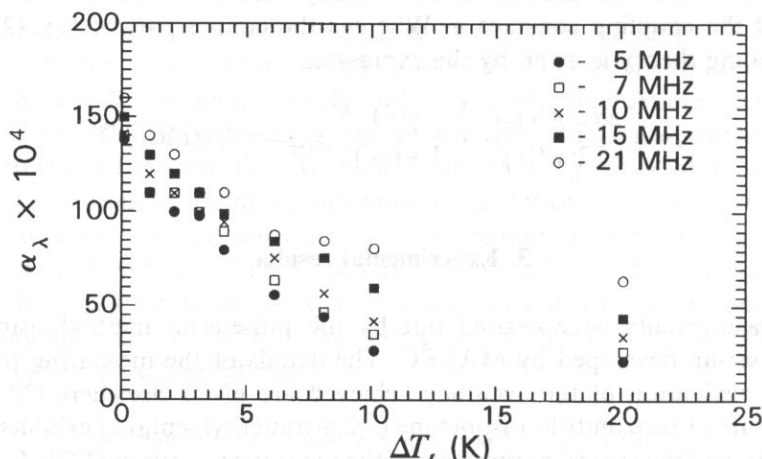

Fig. 3. Absorption coefficient per wavelength versus temperature for different frequencies of the ultrasonic wave.

4. Determination of the collateral thermodynamic parameters

The absorption coefficient measured in experiment is the sum of the critical absorption and the background (Navier-Stokes) absorption, the latter being present even if the critical fluctuations in concentration are absent. The background absorption is described by the well known Stokes-Kirchhoff formula

$$\alpha_\lambda^b \simeq \frac{2\pi^2}{\rho u^2(\omega)}\left[\frac{4}{3}\eta_s+\zeta_0\right]f, \tag{4.1}$$

where ζ is the bulk viscosity at equilibrium. Regrettably, it was not possible to make use of Eq. (4.1) for the determination of α_λ^b since the values of the η_s and ζ_0 for the benzonitrile+isooctane system were unavailable. However, α_λ^b could be determined from Eq. (2.10) which predicts a linear relationship between (α_c/f^2) and $f^{-1.06}$, as shown in Fig. 4. Linear regression analysis applied to the point in Fig. 4 led to the slope $S=2.68\times10^{-5}\,\text{m}\cdot\text{s}^{-0.94}$ and intercept $b=164\times10^{-15}\,\text{s}^2\text{m}^{-1}$. Since $b=\alpha_\lambda^b/f_u$, we have $\alpha_\lambda^b=7.8\times10^{-11}f$.

The adiabatic thermal expansion coefficient can be determined if the temperature dependence of the density is given in the form $\rho=C_1+C_2\epsilon+C_3\epsilon^{1-\alpha}$. Exact measure-
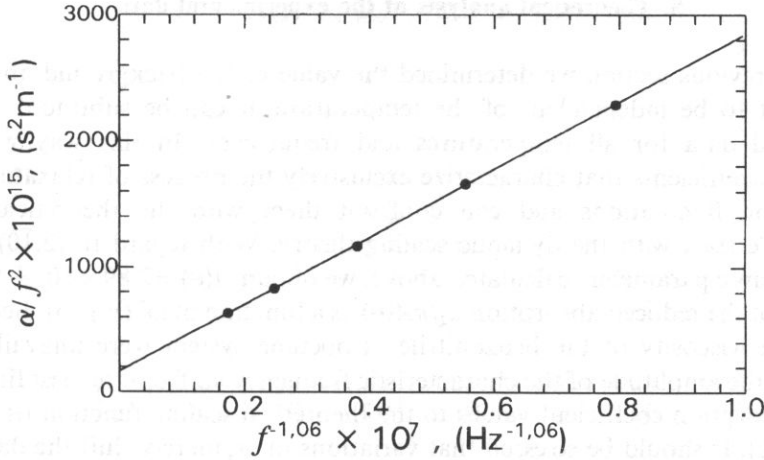
Fig. 4. α_c/f^2 as a function of $f^{-1.06}$ for critical benzonitrile+isooctane mixture.

ments of the density of benzonitrile+isooctane mixtures have been performed by MILLER et al. [22] leading to $\rho\,(\mathrm{kg\cdot m^{-3}})=807.086-294\,\epsilon+13\epsilon^{1-\tilde{\alpha}}$. Together with the relations $\alpha_{Pc}=(\tilde{\alpha}-1)C_3/\rho_c T_c$ and $\alpha_{Pb}=-C_2/\rho T_c$, this gives $\alpha_{Pc}=-0.49\times10^{-4}\,\mathrm{K^{-1}}$ and $\alpha_{Pb}=12.48\times10^{-4}\,\mathrm{K^{-1}}$.

The critical part of the specific heat at constant pressure can be determined from the relation

$$\frac{dT_c}{dP}=\frac{T_c\alpha_{Pc}}{\rho_c c_{Pc}}. \tag{4.2}$$

Using the values $\rho_c=807.086\ \mathrm{kg\cdot m^{-1}}$ and $dT_c/dP=-11.8\times10^{-8}\ \mathrm{K\cdot Pa^{-1}}$ [22], we got $c_{Pc}=0.15\times10^3\ \mathrm{J\cdot kg^{-1}K^{-1}}$.

The value of ξ_0 was calculated assuming the two-scale factor universality that leads to

$$R_\xi=\frac{c_{Pc}\rho_c\tilde{\alpha}\xi_0^3}{k_B}, \tag{4.3}$$

where R_ξ is a dimensionless constant equal to 1.95×10^{-2} as determined from the renormalization group theory [23]. Eq. (4.3) leads to $\xi_0=2.72\times10^{-10}$ m.

We still have to determined the coupling constant g and the regular part of the specific heat at constant pressure c_{Pb}. Here we can make use of the fact that the quotient g/c_{Pb} appears both in the expression for S [Eq. (2.10)] and in the formula (2.5). On solving this set of equations we get $g=-0.678$ and $c_{Pb}=3.29\times10^3$ $\mathrm{J\cdot kg^{-1}K^{-1}}$. The minus sign preceding the value of the adiabatic coupling constant comes from the negative value of dT_c/dP. Thus, in the benzonitrile+isooctane mixture the changes in the critical temperature are in opposite phase to the changes in the pressure.

5. Theoretical analysis of the experimental data

In the previous section we determined the value of the background absorption. Assuming it to be independent of the temperature, it can be subtraced from the experimental data for all temperatures and frequencies. In this way we obtain absorption coefficients that characterize exclusively the process of relaxation of the concentration fluctuations and can confront them with the theoretical scaling function. We start with the dynamic scaling theory. With regard to (2.10) and the thermodynamic parameters calculated above, we obtain $A(\epsilon) = 2.89 \times 10^{-3}$. With this value we plot the reduced absorption $\alpha_\lambda/\pi A(\epsilon)$ as a function of ω^* (Fig. 5). Because the data for the viscosity of the benzonitrile+isooctane system were unavailable, we detemrined the amplitude of the characteristic frequency ω_0 from the best fit between reduced absorption coefficient values to the theoretical scaling function $G(\omega^*)$ given by Eq. (2.11). It should be stressed that variations in ω_0 merely shift the data to the right or left, whereas their displacement upwards or downwards is governed by the value of the critical amplitude. The least-squares method in the form of the CURFIT procedure [24] yielded a characteristic frequency of $\omega_0 = 3.89 \times 10^{10}$ s^{-1}.
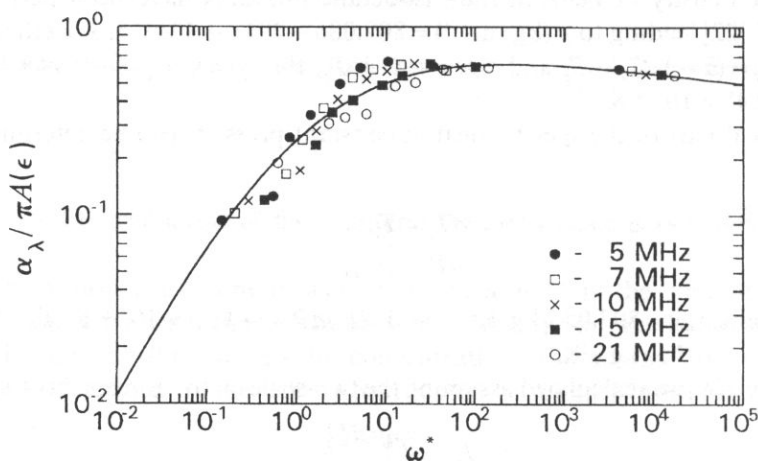
Fig. 5. $\alpha_\lambda/\pi A(\epsilon)$ versus the reduced frequency ω^* for the benzonitrile+isooctane mixture. The solid line represents the scaling function $G(\omega^*)$ given by Eq. (2.11).

Figure 5 shows good agreement between experimental results and the theoretical scaling function of Bhattacharjee and Ferrell within the whole range of the reduced frequencies.

Let us now pass on to the mode-coupling theory. We have got all the values of the thermodynamic parameters required for the detailed analysis of the critical amplitude $A(\epsilon)$. Fig. 6 shows the values of $A(\epsilon)$ determined from Eq. (2.4) *versus* ϵ; $A(\epsilon)$ is found to diverge, but insiginifcantly, from the exponential const $\epsilon^{-\tilde{a}}$ (dashed line in Fig. 6). This is due to the circumstances that the critical part of the specific heat at constant
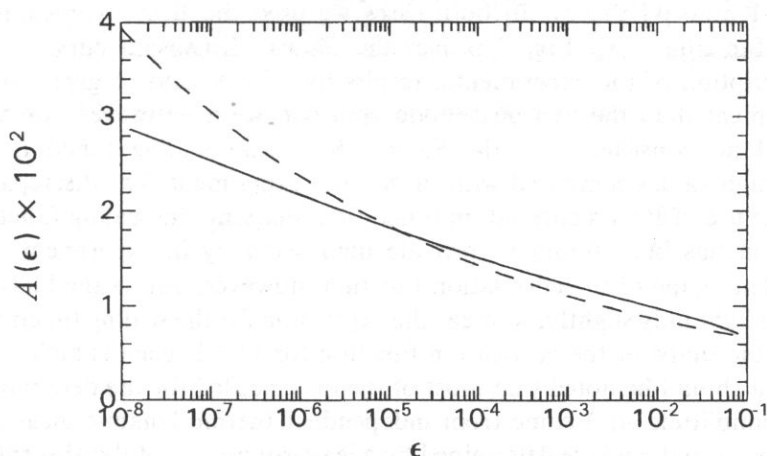
Fig. 6. $\alpha_\lambda/\pi A(\epsilon)$ *versus* the reduced temperature ϵ for the benzonitrile+isooctane mixture. The dashed line shows the dependence on const $\epsilon^{-\tilde{\alpha}}$.

pressure c_{Pc} of the benzonitrile+isooctane mixture is relatively small compared with the regular part c_{Pb}. In mixtures where c_{Pc} and c_{Pb} are similar in magnitude (e.g. aniline—cyclohexane [25]) the critical amplitude $A(c)$ remains practically constant because in Eq. (2.4) the quantities divergent to infinity — c_P in the denominator, $\epsilon^{-\tilde{\alpha}}$ in the numerator — cancel out mutually. The temperature dependence of the acoustic wave velocity affects the critical amplitude $A(\epsilon)$ but slightly.

Figure 7 represents the dependence of the expression $\alpha_\lambda/\pi A(c)$ on ω^*. The dashed line gives the scaling function $I^{(2)}(\omega^*)$ proposed by Kawasaki in the approximation of two heat-mode contributions, whereas the solid line gives the sum $I^{(2)}(\omega^*)+I^{(4)}(\omega^*)$ of
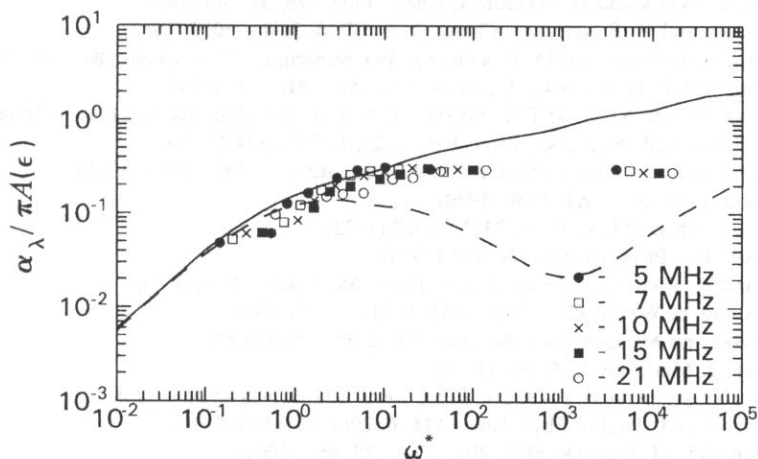

Fig. 7. $\alpha_\lambda/\pi A(\epsilon)$ *versus* the reduced frequency for the benzonitrile+isooctane mixture; dashed line — the scaling function $I^{(2)}(\omega^*)$, solid line — the sum $I^{(2)}(\omega^*)+I^{(4)}(\omega^*)$.

the Shiwa−Kawasaki theory. In both cases we used the Bray expression for the correlation function $X(x)$. Fig. 7 proves the Shiwa−Kawasaki curve to provide a good description of the experimental results for $\omega^* < 50$ and to give a somewhat better agreement than the two heat-mode approximation. However, for higher ω^* there is still no consistence — the Shiwa−Kawasaki scaling function leads to excessively high values compared with those from experiment. The discrepancy may be due to the use of Bray's correlation function in deriving the scaling function. The Bray function has been found to provide high accuracy in experiments on light scattering. The shape of the correlation function, however, affects the half-width of the scattered light only slightly, whereas the expression for the scaling function is very sensitive to the shape of the correlation function for $k\xi > 1$ when is high.

Finally, it should be noted that most of the data needed for the determination of the critical amplitude $A(\epsilon)$ come from independent thermodynamic measurements, whereas only c_{Pb} and g where determined by a least-squares fit of the absorption data to the linear relation between α_c / f^2 and $f^{1.06}$ derived from the dynamic scaling theory. The fact that the critical amplitude determined in this way leads to a correct scaling of the absorption data for the low values of the ω^* points to the validity of new generalized expression for $A(\epsilon)$ given by Eq. (2.4). The discrepancy between the experimental results and the Shiwa−Kawasaki theory at high valeus of ω^*, however, points to the necessity of searching for further modifications of the scaling function. Work in this direction is now under-way.

References

[1]   Y. HARADA, Y. SUZUKI and Y. ISHIDA, J. Phys. Soc. Jpn., **48**, 703 (1980).

[2]   H. TANAKA, Y. WADA and H. NAKAJIMA, Chem. Phys., **75**, 37−43 (1983).

[3]   C.W. GARLAND and G. SANCHEZ, J. Chem. Phys., **79**, 6, 3090−3099 (1983).

[4]   G. JASCHULL, H. DUNKER and D. WOERMANN, Ber Bunsenges. Phys. Chem., **88**, 630−635 (1984).

[5]   M. ŁABOWSKI and T. HORNOWSKI, J. Acoust. Soc. Am., **81**, 1421 (1987).

[6]   I.R. ABDELRAZIQ, S.S. YUN and F.B. STUMPF, J. Acoust. Soc. Am., **88**, 4, 1831−1836 (1990).

[7]   D.M. KROLL and J.M. RUHLAND, Phys. Rev., **A23**, 1, 371−374 (1981).

[8]   R.A. FERRELL and J.K. BHATTACHARJEE, Phys. Rev., **A31**, 3, 1788−1809 (1985).

[9]   K. KAWASAKI, Phys. Rev., **A1**, 1750 (1970).

[10] L. MISTURA, J. Chem. Phys., **57**, 6, 2311−2317 (1972).

[11] I.A. CHABAN, Sov. Phys. Acoust., **21**, 177 (1975).

[12] Y. SHIWA and K. KAWASAKI, Progr. Theor. Phys., **66**, 2, 406−419 (1981).

[13] H. TANAKA and Y. WADA, Phys. Rev., **A32**, 1, 512−524 (1985).

[14] T. HORNOWSKI and M. ŁABOWSKI, Acustica, **72**, 2, 96−100 (1990).

[15] M.E. FISHER, J. Math. Phys., **5**, 944 (1969).

[16] Y. HARADA, Y. SUZUKI and Y. ISHIDA, Phys. Rev., **A21**, 3, 928−931 (1980).

[17] P. TARTAGLIA and J. THOEN, Phys. Rev., **A11**, 6, 2061−2065 (1975).

[18] M.E. FISHER and S.J. LANGER, Phys. Rev. Lett., **20**, 665 (1968).

[19] A. BRAY, Phys. Rev., **B14**, 3, 1248−1270 (1976).

[20] T. HORNOWSKI and M. ŁABOWSKI, Acta Phys. Pol., **A79**, 5, 671−682 (1991).

[21] T. HORNOWSKI, Acta Phys. Pol., **A82**, 6, 961−966 (1992).

[22] B.C. MILLER, E.A. CLERKE and S.C. GREER, J. Phys. Chem., **87**, 6, 1063 – 1066 (1983).

[23] C. BERVILLIÈRE and C. GODRÈCHE, Phys. Rev., **B21**, 11, 5427 – 5431 (1980).

[24] P.R. BEVINGTON, *Data reduction and error analysis for the physical sciences*, McGraw-Hill, New York, 1969.

[25] H. TANAKA, Y. WADA and H. NAKAJIMA, Chem. Phys., **68**, 223 (1982).