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VELOCITY DISPERSION AND ATTENUATION OF ACOUSTIC WAVES IN CRITICAL MIXTURES

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Theoretical considerations on critical ultrasonic dispersion and attenuation in binary liquid mixtures based on the mode-coupling approach and frequency-dependent heat capacity are presented. A general expression for the critical amplitude $A(T)$ in terms of the parameter $d = (\varrho c^0_{v,x}/T\alpha_P)\cdot(dT_c/dP)$ is derived. It is shown that for specific values of d one obtains expressions for $A(T)$ equivalent to those of Fixman, Kawasaki, Mistura and Chaban. Moreover, an experimental test has been carried out on the system methanol-n-hexane showing good agreement between our general expression for $A(T)$ and experimental data.

W pracy zaprezentowano teoretyczne rozważania odnośnie do dyspersji i absorpcji fal ultradźwiękowych w mieszaninach krytycznych na gruncie teorii modów sprzężonych. Wyprowadzono ogólne wyrażenie na amplitudę pochłaniania $A(T)$ w postaci funkcji parametru d zdefiniowanego jako $d = (\varrho c^0_{v,x}/T\alpha_P)\cdot(dT_c/dP)$ i wykazano, że dla określonych wartości d uzyskuje się wyrażenia na $A(T)$ zgodne z teoriami Fixmana, Kawasaki, Mistury i Czabana. Przeprowadzono również weryfikację uzyskanych wyrażeń otrzymując dobrą zgodność z danymi eksperymentalnymi.

1. Introduction

In the theory of critical phenomena, an important role is played by the mode-coupling method, first formulated by KADANOFF and SWIFT [1] and thereupon applied to the solving of various problems of the physics of phase transitions, i.a., that of the acoustic wave propagation in critical mixtures. The most important theories in this field applying the mode-coupling approach are those of KAWASAKI, [2, 3], Mistura [4] and Chaban [5, 6] and, to a lesser degree, that of FIXMAN [7]. These theories lead to expressions for the attenuation α_λ of the acoustic wave (per wave length λ) that can be written in the form $\alpha_\lambda/c^2 = \pi \cdot A(T) \cdot I(\omega^*)$. The scaling function $I(\omega^*)$ is in all cases the same, whereas the amplitudes $A(T)$ differ essentially. Our paper is aimed, i.a., at the elucidation of the source of these differences.

2. Velocity dispersion and attenuation of the ultrasonic waves

Within the framework of mode-coupling theory [4], it can be shown that the excess specific heat at constant pressure related with relaxation of fluctuations in concentration is given by the following expression

$$\langle \delta c_P(\omega^*) \rangle = \frac{k_B T^2}{\pi^2 \varrho} \left(1 - \frac{\eta}{2}\right)^2 \varkappa \left(\frac{\partial \varkappa}{\partial T}\right)^2 \int_0^\infty \frac{y^2 dy}{(1+y^2)^2} \cdot \frac{\omega^*}{K(y) - i\omega^*}, \tag{1}$$

with k_B – Boltzmann's constant, $\varkappa = 1/\xi$ – the inverse correlation of fluctuations in concentration, ϱ – the density of mixture, η – the critical exponent characterizing the deviation of the radial correlation function from the Ornstein-Zernike approximation and $y = k \cdot \xi$. The quantity ω^* is the reduced frequency defined as [8]

$$\omega^* = \omega/\omega_D = 2\pi f/(\omega_0 \varepsilon^{-z\nu}), \tag{2}$$

where ω_D is a temperature-dependent characteristic frequency, related with the concentration- fluctuation lifetime in the critical point of the mixture and given by Stokes-Einstein formula

$$\omega_D = k_B T/3\pi\eta\xi^3 = (k_B T/3\pi\eta\xi_0^3)\varepsilon^{-z\nu}, \tag{3}$$

with $\xi = \xi_0 \varepsilon^{-\nu}$ for the correlation length and $\eta = \eta_0 \varepsilon^{-(z-3)\nu}$ for the shear viscosity. The function $K(y)$ is related with the concentration-fluctuation lifetime $\tau_{\vec{K}}$ by way of the following expression, resulting from dynamical scaling hypothesis:

$$1/\tau_{\vec{K}} = 1/2\, \omega_D K(y). \tag{4}$$

The expression (1) enables us to write the total complex specific heat $\tilde{c}_{P,x}$ at constant pressure in the form

$$\tilde{c}_{P,x} = c^0_{P,x} + i \langle \delta c_P(\omega^*) \rangle = c^0_{P,x} + \Delta(i\omega^*). \tag{5}$$

In addition to the excess specific heat at constant pressure, we have to determine that at constant volume. To this purpose, one can make use of the formula [9]

$$c_{V,x} = c_{P,x} + \frac{[(\partial V/\partial T)_{P,x}]^2}{(\partial V/\partial P)^0_{T,x}}. \tag{6}$$

By the scaling hypothesis [10], the Gibbs thermodynamical potential in the neighbourhood of the critical point is a homogeneous function and thus can be written in the form [11]

$$G(T, x, P) = G_0(T, x, P) + |\varepsilon(P)|^{2-\alpha} f(\Phi/|\varepsilon(P)|^{-\beta}), \tag{7}$$

where α, β are the critical exponents; $\varepsilon(P) = [T - T_c(P)]/T_c$ the so-called reduced distance from the critical point on the temperature-axis; and $\Phi = (x - x_c(P))/x_c$ the ordering parameter. The Gibbs thermodynamical potential thus defined enables us to dertermine various thermodynamical parameters, among which are $(\partial V/\partial P)_{T,x}$,

$(\partial V/\partial T)_{P,x}$ and $c_{P,x}$. At $x = x_c$ we have $f(\Phi/|\varepsilon(P)|^{-\beta}) = \text{const}$, whence

$$c_{P,x} = -T(\partial^2 G/\partial T^2)_{P,x} = A_1|\varepsilon(P)|^{-\alpha} + c^0_{P,x}, \tag{8}$$

$$(\partial V/\partial P)_{T,x} = (\partial^2 G/\partial P^2)_{T,x} = A_1(\partial T_c/\partial P)^2|\varepsilon(P)|^{-\alpha} + (\partial V/\partial P)^0_{T,x}, \tag{9}$$

$$(\partial V/\partial T)_{P,x} = (\partial^2 G/\partial T\partial P)_{P,x} = -A_1(\partial T_c/\partial P)|\varepsilon(P)|^{-\alpha} + (\partial V/\partial T)^0_{P,x}, \tag{10}$$

On insertion of (8), (9), and (10), into Eq. (6) we obtain the specific heat at constant volume in the following form:

$$c_{V,x} = A_1|\varepsilon(P)|^{-\alpha} + c^0_{P,x} + \frac{[A_1(\partial T_c/\partial P)|\varepsilon(P)|^{-\alpha} + (\partial V/\partial T)^0_{P,x}]^2}{-A_1(\partial T_c/\partial P)^2|\varepsilon(P)|^{-\alpha} + (\partial V/\partial P)^0_{T,x}}, \tag{11}$$

The expression (11) can be expanded in a series in $(\partial T_c/\partial P)$, restricting the expansion to quadratic terms and omitting the term proportional to $|\varepsilon(P)|^{-2\alpha}$ which is much smaller than the others. We thus obtain

$$c_{V,x} \approx A_1|\varepsilon(P)|^{-\alpha}\left\{1 + 2\frac{(\partial V/\partial T)^0_{P,x}}{(\partial V/\partial P)^0_{T,x}}\cdot\frac{dT_c}{dP} + \left[\frac{(\partial V/\partial T)^0_{P,x}}{(\partial V/\partial P)^0_{T,x}}\cdot\frac{dT_c}{dP}\right]^2\right\} + c^0_{P,x} + \frac{[(\partial V/\partial T)^0_{P,x}]^2}{(\partial V/\partial P)^0_{T,x}}. \tag{12}$$

On introducing the notation

$$c^0_{V,x} = c^0_{P,x} + \frac{[(\partial V/\partial T)^0_{P,x}]^2}{(\partial V/\partial P)^0_{T,x}}, \tag{13}$$

$$d = \frac{c^0_{V,x}\varrho}{T\alpha_p}\cdot\frac{dT_c}{dP} \tag{14}$$

and applying the thermodynamical identity [12]

$$\frac{(\partial V/\partial T)^0_{P,x}}{(\partial V/\partial P)^0_{T,x}} = -\frac{\varrho}{T\alpha_p}(c^0_{p,x} - c^0_{v,x}) = -\frac{c^0_{V,x}\varrho}{T\alpha_p}(\gamma - 1), \tag{15}$$

we obtain

$$c_{V,x} \approx A_1[1 - d(\gamma - 1)]^2|\varepsilon(P)|^{-\alpha} + c^0_{V,x} = A_2|\varepsilon(P)|^{-\alpha} + c^0_{V,x}. \tag{16}$$

Comparing Eqs. (8) and (16) we get the ratio of the excess specific heats at constant pressure and constant volume, two quantities related with concentration-fluctuation relaxation:

$$\langle \delta c_{V,x}(\omega^*)\rangle = (A_1/A_2)\langle \delta c_{P,x}(\omega^*)\rangle = (A_1/A_2)\Delta(i\omega^*), \tag{17}$$

where

$$A_1/A_2 = [1 - d(\gamma - 1)]^2. \tag{18}$$

Thus, the total complex specific heat at constant volume takes the form

$$\tilde{c}_{V,x} = c^0_{V,x} + (A_1/A_2)\Delta(i\omega^*). \tag{19}$$

With the complex specific heats available – Eqs. (4) and (18) – we are in a position to determine the complex propagation velocity $\tilde{c}$ of ultrasonic waves from the formula

$$\tilde{c}^2 = \frac{T}{\varrho^2}\left(\frac{\partial P}{\partial T}\right)^2_{\varrho,x} \frac{\tilde{c}_{P,x}}{\tilde{c}_{V,x}(\tilde{c}_{P,x} - \tilde{c}_{V,x})}. \tag{20}$$

We are now able to determine $\tilde{c}^{-1}$, inserting the expressions (5) and (19) into (20) and expanding the expression thus obtained in a Taylor series in $\Delta(i\omega^*)$. On restricting ourselves to the first-order terms, we get

$$\tilde{c}^{-1} \approx c_0^{-1}\left[1 + \frac{(A_1/A_2)\gamma^2 - 2(A_1/A_2)\gamma + 1}{2c^0_{P,x}(\gamma - 1)}\Delta(i\omega^*)\right], \tag{21}$$

where

$$c_0^{-1} = \left[\frac{T}{\varrho^2}\left(\frac{\partial P}{\partial T}\right)^2_{\varrho,x} \frac{c^0_{P,x}}{c^0_{V,x}(c^0_{P,x} - c^0_{V,x})}\right]^{-1/2}. \tag{22}$$

With regard to (18), the numerator of Eq. (22) takes the form

$$(A_1/A_2)\gamma^2 - 2(A_1/A_2)\gamma + 1 = (\gamma - 1)^2 f(d), \tag{23}$$

where the function $f(d)$ is defined as the sum of the following two polynomials

$$F_1(d) = \gamma^2(d - 1/\gamma)^2 \tag{24}$$

$$F_2(d) = -2d\gamma[d - 1/(\gamma - 1)]. \tag{25}$$

With $f(d)$ defined as above, we can express the complex velocity of propagation of ultrasonic waves in critical mixtures as follows:

$$\tilde{c}^{-1} = c_0^{-1}\left[1 + \frac{f(d)(\gamma - 1)}{2c^0_{P,x}}\Delta(i\omega^*)\right]. \tag{26}$$

On the other hand, the complex velocity is

$$\tilde{c}^{-1} = c^{-1} + i\omega^{-1}\alpha, \tag{27}$$

whence, with the real and imaginary parts, we finally obtain the following expressions for the velocity dispersion $\Delta c/c_0$ and attenuation coefficient α of acoustic waves in critical mixtures:

$$\alpha\lambda/c_0^2 = \pi A(T) I(\omega^*), \tag{28}$$

$$\Delta c/c_0 = -\frac{1}{2} A(T) J(\omega^*), \tag{29}$$

with the coefficient $A(T)$ and the functions $I(\omega^*)$ and $J(\omega^*)$ given by

$$A(T) = \frac{k_B T^2(\gamma-1)}{\pi^2 \varrho c_0^2 c_{P,x}^0}\left(1-\frac{\eta}{2}\right)^2 \varkappa\left(\frac{\partial \varkappa}{\partial T}\right)^2 f(d), \tag{30}$$

$$I(\omega^*) = \mathrm{Im}\left[\frac{(\gamma-1)f(d)\Delta(i\omega^*)}{c_{P,x}^0 c_0^2 A(T)}\right] = \int_0^\infty \frac{y^2 dy}{(1+y^2)^2}\cdot\frac{\omega^* K(y)}{K^2(y)+(\omega^*)^2}, \tag{31}$$

$$J(\omega^*) = \mathrm{Re}\left[\frac{(\gamma-1)f(d)\Delta(i\omega^*)}{c_{P,x}^0 c_0^2 A(T)}\right] = \int_0^\infty \frac{y^2 dy}{(1+y^2)^2}\cdot\frac{(\omega^*)^2}{K^2(y)+(\omega^*)^2}. \tag{32}$$

The coefficient $A(T)$ determining the amplitude of the fluctuations in concentration in the critical point, can be expressed in a different way making use of the scaling relation

$$\varkappa = \xi^{-1} = \xi_0^{-1}\varepsilon^{\nu}. \tag{33}$$

for the correlation length of fluctuations in concentration [9]. This leads to the following expression:

$$A(T) = \frac{k_B(\gamma-1)\nu^2}{\pi^2 \varrho c_0^2 c_{P,x}^0 \xi_0^3}\left(1-\frac{\eta}{2}\right)^2 f(d)\varepsilon^{-\alpha}. \tag{34}$$

3. Analysis and discussion

The formulae (31), (32) and (33) derived by us are general expressions for the propagation velocity and attenuation coefficient of acoustic waves in critical mixtures. The expressions for the attenuation of acoustic waves derived within the framework of the theories of Fixman, Mistura, Kawasaki and Chaban can be shown to represent particular cases of our expressions. To this aim, we have to investigate the properties of the function $f(d)$. As already stated, $f(d)$ is the sum of polynomials of the second degree $F_1(d)$ and $F_2(d)$. Their graphs have the form of the parabol as shown in Fig. 1, the analysis of the latter enables us to distinguish three cases:

i) $d = 0$, implying $(\partial T_c/\partial P) = 0$. In this particular case we have $F_1(d) = 1$, $F_2(d) = 0$ and $f(d) = 1$ thus obtaining an expression for $A(T)$ in accordance with the theories of Fixman and Kawasaki;

ii) $d = 1/(\gamma-1)$, implying $(\partial T_c/\partial P = T\alpha_P/[\varrho(c_{P,x}^0 - c_{V,x}^0)]$. We thus have $F_1(d) = 1/[(\gamma-1)^2]$, $F_2(d) = 0$ and $f(d) = 1/(\gamma-1)^2]$. The expression for $A(T)$ is in this case in accordance with the theory of Mistura.

iii) $0 < d < d|_{F_1(d) \gg F_2(d)}$, giving $f(d) \approx F_1(d) = (1-d\gamma)^2$. The expression for $A(T)$ now takes a form in agreement with the theory of Chaban.

The relations thus obtained are assembled in Table 1.

For the theories of Kawasaki, Mistura and Chaban the form of $K(y)$ is given by

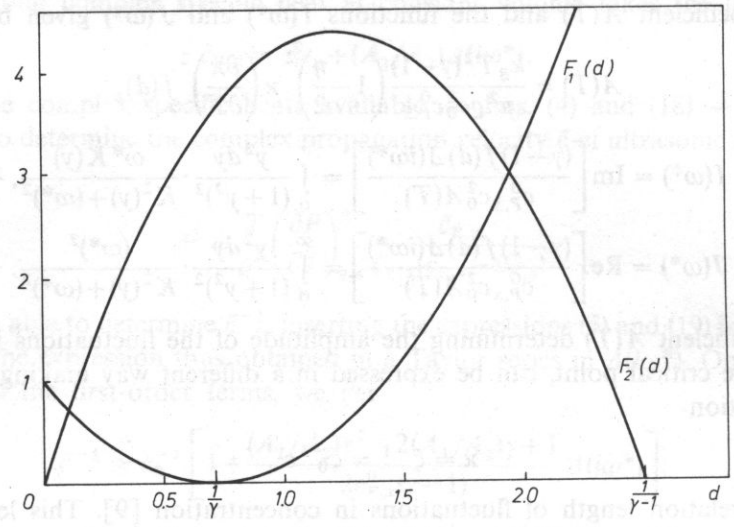

FIG. 1. Shape of the functions $F_1(d)$ and $F_2(d)$ for $\gamma = 1.4$

Table 1

Theory	d	$K(y)$	A(T)
FIXMAN [7]	0	$y^2(1+y^2)$	$\frac{k_B(\gamma-1)v^2}{\pi^2\varrho c_0^2 c_{P,x}\xi_0^3}\varepsilon^{-\alpha}$
KAWASAKI [2]	0	$K_W(y)$	$\frac{k_B(\gamma-1)v^2}{\pi^2\varrho c_0^2 c_{P,x}\xi_0^3}\varepsilon^{-\alpha}$
MISTURA [5]	$\frac{1}{\gamma-1}$	$K_W(y)$	$\frac{k_B v^2}{\pi^2\varrho c_0^2 c_{P,x}\xi_0^3(\gamma-1)}\left(1-\frac{\eta}{2}\right)^2\varepsilon^{-\alpha}$
CHABAN [6]	$0 < d < 0{,}01$	$K_W(y)$	$\frac{k_B(\gamma-1)v^2}{\pi^2\varrho c_0^2 c_{P,x}\xi_0^3}\left(1-\frac{\varrho c_{P,x}^0}{\alpha_p T}\frac{\partial T_c}{\partial P}\right)^2\varepsilon^{-\alpha}$

the Kawasaki function [4]

$$K_W(y) = \frac{3}{4}[1+y^2+(y^3-1/y)\arctan y]. \tag{35}$$

In order to check the relationships derived by us, we made use of the experimental results for acoustic wave attenuation in the methanol-cyclohexane critical mixture published in Ref. [13]. The literature [9, 13–15] moreover contains experimental data for $c_{P,x}^0$, $c_{V,x}^0$, α_P, $(\partial T_c/\partial P)$, ξ_0 and ϱ for the above mixture. The parameter d determined with these data amounts to 1.11. For ω_0 we assumed 1.64×10^{12} Hz after the authors of Ref. [13]. Figs. 2–5 show the experimental data in

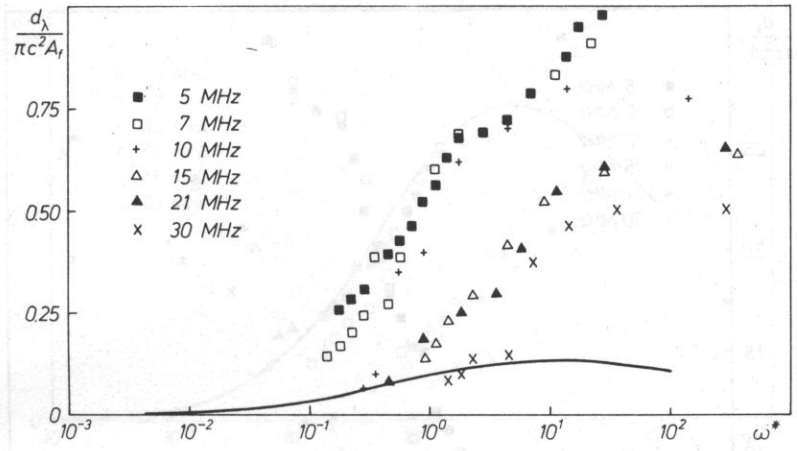

FIG. 2. $\alpha_\lambda/(\pi c^2 A)$ vs. ω^* for the critical methanol-cyclohexane mixture, for $A(T)$ calculated according to the theory of Fixman. The experimental data are taken from Ref. [13]

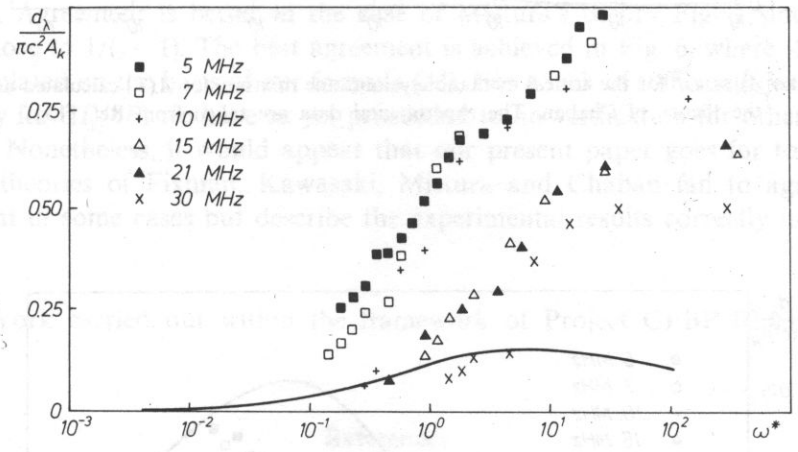

FIG. 3. $\alpha_\lambda/(\pi c^2 A)$ vs. ω^* for the critical methanol-cyclohexane mixture, for $A(T)$ calculated according to the theory of Kawasaki. The experimental data are taken from Ref. [13]

the form of α_λ $(\pi c_0^2 A)$ versus ω^*, with values of A corresponding to the theories of Fixman, Kawasaki, Mistura and Chaban, respectively. The results shown in Fig. 6 are those obtained with our formula (34). Everywhere, the continuous curves show the scaling function given by Eq. (31). Obviously, agreement between the theories of Fixman (Fig. 2), Kawasaki (Fig. 3) and Chaban (Fig. 4) on the one hand and the experimental results on the other is very weak, this is by no means surprising in the

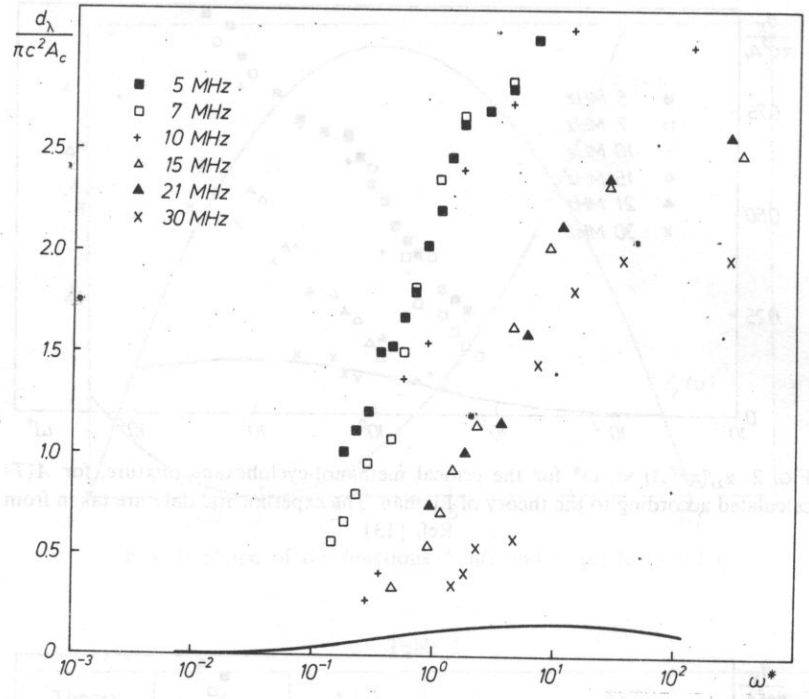

FIG. 4. $\alpha_\lambda/(\pi c^2 A)$ vs. ω^* for the critical methanol-cyclohexane mixture, for $A(T)$ calculated according to the theory of Chaban. The experimental data are taken from Ref. [13]

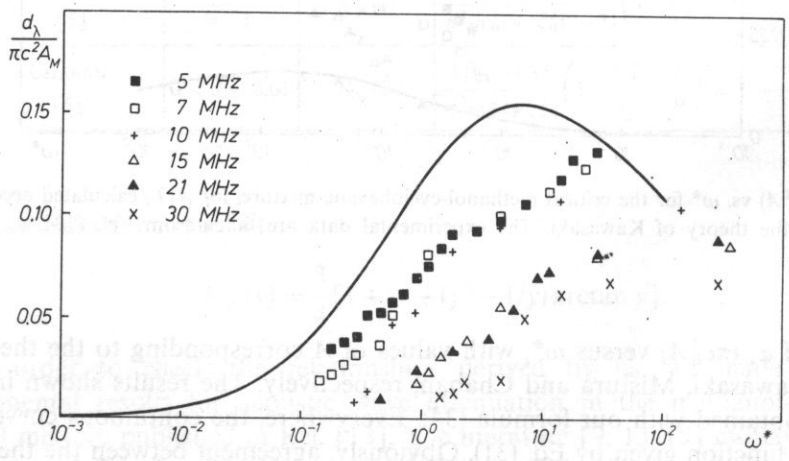

FIG. 5. $\alpha_\lambda/(\pi c^2 A)$ vs. ω^* for the critical methanol-cyclohexane mixture, for $A(T)$ calculated according to the theory of Mistura. The experimental data are taken from Ref. [13]

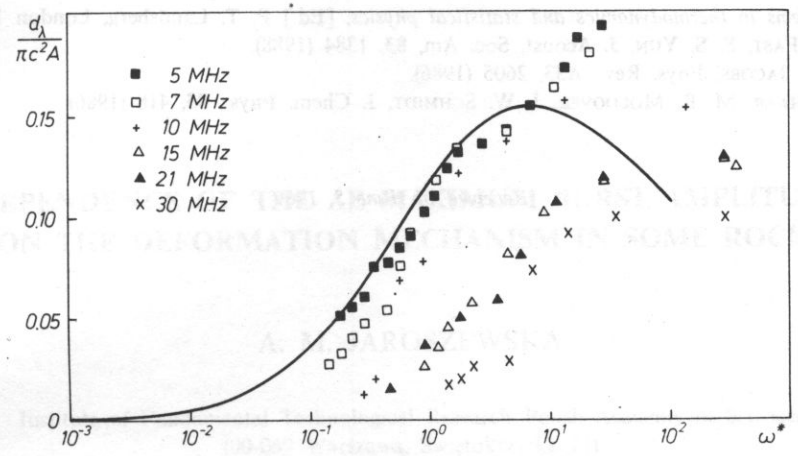

FIG. 6. $\alpha_\lambda/(\pi c^2 A)$ vs. ω^* for the critical methanol-cyclohexane mixture, for $A(T)$ calculated with our formula (34). The experimental results are taken from Ref. [13]

light of our preceding considerations, since the parameter d differs from zero markedly. Agreement is better in the case of Mistura's theory Fig. 5 since d has a value close to $1/(\gamma-1)$. The best agreement is achieved in Fig. 6, where $A(T)$ has been calculated on the basis of our formula (34). For a lack of sufficiently exact data (espacially for $\partial T_c/\partial P$) we have as yet proceeded to no verification for other critical mixtures. Nonetheless, it would appear that our present paper goes for to explain why the theories of Fixman, Kawasaki, Mistura and Chaban fail to agree with experiment in some cases but describe the experimental results correctly in others.

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