

Acoustic relaxation in the critical region of water

N. F. Erokhin

Taganrog Pedagogical Institute

(Submitted 7 May 1980)

Pis'ma Zh. Eksp. Teor. Fiz. **31**, No. 12, 763–767 (20 June 1980)

The frequency dependence of the absorption of sound in the critical region of water was studied for the first time. The absorption for the critical isochor and isotherm can be fitted on one universal curve when the critical index of the coexistence curve does not agree with the predictions of the scaling theory.

PACS numbers: 62.60. + v, 64.60.Fr

The results of a dynamic scaling theory¹ and an experiment using simple (Xe) liquids² and binary mixtures (nitroethane-isooctane)³ have established a universal dependence of the excess absorption coefficient of sound (α_η, λ) on the reduced frequency (ω^*). The theory, however, has not been tested using complex, one-component systems that can influence the results of molecular internal degrees of freedom. In particular, the relaxation processes in the critical region of a specific system such as water hitherto have not been studied because of the difficulty of setting up an acoustic (spectroscopic) experiment at high temperatures and pressures ($T_c = 647.38$ K, $P_c = 22.124$ MPa).

The excess absorption coefficient per wavelength, governed by the volume viscosity,⁴ can be expressed in the following form for the critical isochor of a one-component liquid:

$$\alpha_{\eta} \cdot \lambda = A(T) \int_0^{\infty} \frac{y^2}{(1+y^2)^2} \frac{K(y)\omega^*}{K^2(y) + \omega^{*2}} dy, \quad (1)$$

where $\omega^* = \omega/\omega_c$, ω_c is the frequency of the external field, $\omega_c = (kT/3\pi\eta^*r_c^3)$ is the characteristic relaxation frequency which is uniquely determined by the equilibrium correlation of the fluctuations r_c , $K(y)$ is the Kawasaki-Ferrel function⁴ which depends on the wave number q and r_c ($y = qr_c$), and $A(T)$ is a function that depends weakly on the approach to the critical point whose explicit form is given in Ref. 1.

Below we discuss the results of measuring the absorption coefficient of ultrasound waves in terms of the dynamic scaling theory.¹ The absorption coefficient was measured along the critical isochor and the critical isotherm of water by using the experimental setup described elsewhere⁵ and the method of continuous Frei interferometer. The frequency dependence of the absorption coefficient was measured in the 0.48 to 10.38-MHz range with an error ≤ 10 –15%. We were able to measure the absorption coefficient only for the 0.48 to 3.55-MHz frequencies because of anomalously large increase of the absorption coefficient in the immediate vicinity of the critical point. The accuracy of the thermostatic control of the water sample was ± 0.01 K.

Figure 1 shows the dependence of the excess absorption coefficient of ultrasound

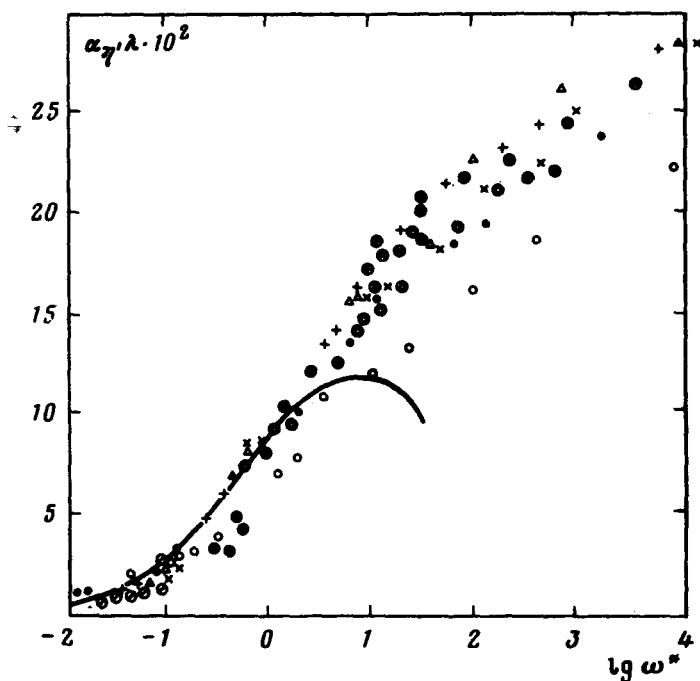


FIG. 1. Excess absorption coefficient of ultrasound per wavelength as a function of the reduced frequency ω^* : (for the critical isochor (●) 0.48 MHz, (+) 1.47, (Δ) 2.55, (\times) 3.55 MHz; for the critical isotherm (○) 0.48, (⊙) 1.47, (⊗) 2.55, (\times) 3.55, (⊙) 10.38 MHz).

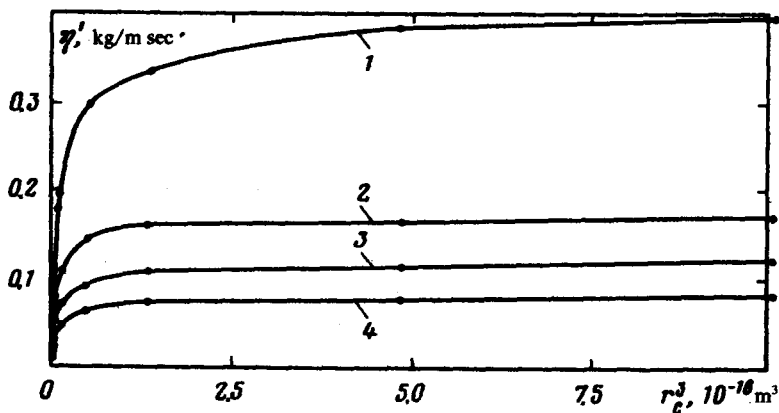


FIG. 2. Dependence of the volume viscosity on the correlation radius for the critical isochor of water.

per wavelength on the reduced frequency along the critical isochor of water for the frequencies: \bullet , 0.48; $+$, 1.47; Δ , 2.55; \times , 3.55 MHz. To calculate the wavelength, we used the data for the dispersion of sound velocity obtained earlier by us.⁵ We can easily see that the experimental data for α_η, λ , which can be fitted on one universal curve (within the limits of random scattering of data for different frequencies and temperatures), are a function of the reduced frequency in a wide variation range of ω^* (six orders of magnitude). This confirms the predictions of the dynamic similarity theory concerning the existence of characteristic relaxation frequency ω_c , which is uniquely related to the equilibrium correlation radius. For $\omega^* \gg 1/\alpha_\eta, \lambda$ must be independent of the approach to the critical point. A tendency for such behavior is evident in Fig. 1. A calculation based on the Kawasaki theory (1) (solid curve) is in satisfactory (quantitative) agreement with the experimental values of α_η, λ for $\omega^* < 10$. A calculation of expression (1) was carried out on a computer (the calculation is analogous to that in Ref. 5 for the dispersion of sound velocity). For $\omega^* > 10$ the theory⁴ is in qualitative disagreement with the experiment, which is attributable to the use of incorrect Ornstein-Zernike correlation function¹ in deriving Eq. (1).

The results of measurements of the excess absorption coefficient for the critical isotherm can be represented in the $\alpha_\eta, \lambda = f(\omega^*)$ coordinates. Since $\Delta\rho \sim t^\beta$ (static scaling hypothesis⁶), we can represent the characteristic frequency in the form

$$\omega_c \sim \Delta\rho^{\frac{2-\alpha}{\beta}}, \quad (2)$$

where $\Delta\rho = (\rho - \rho_K)/\rho_K$ is the relative density, $t = (T_K - T)/T$ is the relative temperature, and α and β are the critical indices of specific heat and of the coexistence curve. We selected the value of $\beta = 0.38$ by varying according to the best fit the α_η, λ data for the critical isochor and the critical isotherm. The same value of β was obtained in a calculation performed by us using the PVT data for the water in the range $10^{-4} < t < 10^{-1}$. However, the theoretical and experimental results obtained by using simple liquids¹ give the most probable value $\beta = 0.34$. Such difference, which is well

outside the error limits of the value of β , is not fully understood. We took the value $\alpha = 0.11$ from the results of measuring the velocity of sound in water,⁵ which coincides with the recommended value.¹ The values of α_η and λ are shown in Fig. 1 for the critical isotherm of water for the following frequencies: ●, 0.48; ⊕, 1.47; △, 2.55; ⊗, 3.55; ○, 10.38 MHz. We can see that the values of the excess absorption coefficient for the critical isochor and the critical isotherm are satisfactorily fitted on the universal curve. The proportionality (2) breaks down in a narrow region in the immediate vicinity of the critical point, which makes it impossible to calculate ω^* (the maximum calculated approximation of the critical point $\Delta\rho = 0.018$). The indicated frequency range (0.48–10.38 MHz) proved to be insufficient for determining the relaxation mechanism in the critical region of water. To obtain a full picture of the relaxation mechanism, we must study the absorption and velocity of sound using the methods of optical-shift spectroscopy.⁷

For the one-component liquids the volume viscosity depends on $r_c (\eta' \sim r_c^3)$ at low frequencies; on the other hand, as $\omega \rightarrow \infty$ it depends only on the frequency ($\eta' \sim \omega^{-1}$).¹ These results are also valid for water. Figure 2 shows the dependence of volume viscosity on r_c for the critical isochor of water (η' was calculated from the measurements of excess absorption⁸). Curves 1, 2, 3, and 4 correspond to the 0.48, 1.47, 2.55, and 3.55-MHz frequencies.

I thank M. A. Anisimov, V. A. Solov'ev, and V. P. Romanov for their useful remarks and attention to this investigation.

¹M. A. Anisimov, Usp. Fiz. Nauk **114**, 249 (1974) [Sov. Phys. Usp. **17**, 722 (1974)].

²C. Garland, D. Eden, and L. Mistura, Phys. Rev. Lett. **25**, 1161 (1970).

³M. A. Anisimov, V. P. Voronov, V. M. Malyshev, and V. V. Svadkovskii, Pis'ma Zh. Eksp. Teor. Fiz. **18**, 224 (1973) [JETP Lett. **18**, 133 (1973)].

⁴K. Kawasaki, Phys. Rev. **A1**, 1750 (1970).

⁵N. F. Erokhin and B. I. Kal'yanov, TVT **1**, 290 (1979).

⁶V. L. Pokrovskii, Usp. Fiz. Nauk **94**, 127 (1968) [Sov. Phys. Usp. **11**, 66 (1968)].

⁷Spektroskopiya opticheskogo smeshcheniya i korrelyatsiya fotonov (Spectroscopy of the Optical Shift and Photon Correlation), ed. by G. Kamins, Mir, Moscow, 1978.

⁸Physical Acoustics, Vol. 7, ed. by W. Mason, Academic Press, NY, 1970.