

## ACOUSTIC PROPERTIES OF LIQUID SYSTEMS NEAR THE CRITICAL TEMPERATURE

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Making use of acoustic spectroscopy methods, the sound attenuation factor and the sound propagation velocity in liquid systems have been studied in a wide range of frequencies, concentrations, and temperatures, including a neighborhood of the critical consolute temperature (CCT). A relaxation interval of sound attenuation has been shown to exist for studied solutions with critical concentration at frequencies lower than 300 MHz when approaching CCT. This interval is caused by creation and decay of critical fluctuations. The relaxation time of those processes, being the averaged lifetime of concentration fluctuations, increases when approaching CCT. The obtained data qualitatively agree with conclusions of dynamical theory of critical phenomena.

Today, a study of critical phenomena in liquid systems remains one of the challenging problems of the condensed matter physics [1, 2]. Investigations of various steady-state properties of those systems near the critical point are the most intense, and great advances in this direction have been achieved [3]. At the same time, there are a few papers devoted to the experimental study of liquid transport properties near critical points, especially by acoustic methods, most of them being carried out in a narrow frequency range. Therefore, the aim of this work is to study the attenuation factor and the sound propagation velocity in various liquid systems near the phase transition point, in wide frequency and temperature intervals, including a close neighborhood of critical temperature.

Liquid systems of different origins have been selected as subjects of inquiry, namely, a binary solution nitromethane — *n*-amyl alcohol, with the mole fraction of *n*-amyl alcohol being of 0.1, 0.3, 0.384 (the critical value), 0.5, and 0.7; a binary solution nitrobenzene—hexane, with the mole fraction of nitrobenzene being of 0.3, 0.4 (the critical value), 0.5, and 0.7; and a nematic liquid crystal 4-pentyl-4'-cyanobiphenyl (5CB). Binary solutions were investigated at temperatures higher than CCT ( $T > T_c$ ).

The sound propagation velocity  $c$  and the amplitude attenuation factor  $\alpha$  in all the liquids concerned were measured by the pulse-phase method in the temperature interval from  $T_c$  to 323 K and in the frequency interval

$f = 5 \div 2500$  MHz. The measurements of  $c$  and  $\alpha$  were carried out according to methods described in [4]. Below, we indicate some features of the acoustic experiment procedure in the case of investigating liquids near a critical temperature. The liquid with critical concentration was poured into an acoustic cell immersed in water, which fills the glass tank covered by heat insulator to reduce the temperature gradient. Temperature stabilization was done with the help of a U-10 thermostat. The error of temperature measurements was of 0.05 °C. The room temperature was kept constant with an accuracy of 0.5 °C.

The temperature stabilization of the system with an accuracy of 0.05 °C was carried out during 1–4 hours, depending on the distance from  $T_c$ . Provided that such conditions for an acoustic experiment are fulfilled, it made possible to measure the sound attenuation factor near the phase transition point with an error of 2–7%, and the sound propagation velocity with an error of 0.5% [4].

In the case of binary solutions, a drastic increase of the amplitude factor of sound attenuation was observed, when approaching  $T_c$ . The temperatures, at which the sound attenuation was maximal, were taken as critical ones. In so doing, the CCT for the system nitromethane — *n*-amyl alcohol was established to be  $T_c = 300.95$  K, and for nitrobenzene — hexane,  $T_c = 293.9$  K. A substantial enhancement of sound attenuation was also observed near the temperature of the nematic–isotropic-liquid phase transition, where an essential growth of the molecular orientation fluctuations takes place due to the spontaneous appearance of a direction of orientational molecular ordering [3]. The temperature, at which the maximal value of the attenuation factor was measured, was taken as the phase transition temperature, and, for 5CB,  $T_c = 307.85$  K.

The studies of the temperature dependence of the sound propagation velocity have not revealed essential anomalies near the critical temperature. It was found that the sound velocity decreases linearly with the temperature growth for the solutions nitromethane —

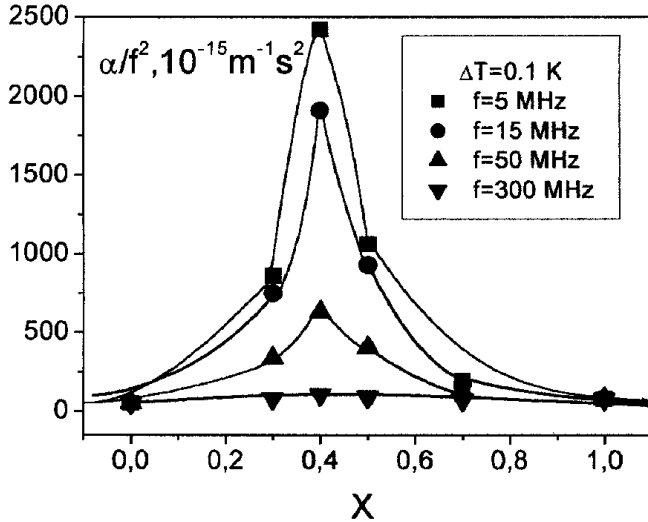


Fig. 1. Concentration dependences of the sound attenuation value  $\alpha f^{-2}$  in nitrobenzene–hexane solution at various frequencies ( $X$  is a molar fraction of nitrobenzene)

*n*-amyl alcohol and nitrobenzene–hexane. In the solutions concerned, the sound propagation velocity does not depend on frequency, within the limits of measurement errors, in the frequency interval of 5–300 MHz. At frequencies higher than 300 MHz, a dispersion of the sound velocity of about 3.5% is observed in the solutions under investigation, which diminishes when moving apart from CCT.

In Fig. 1, the dependences of the sound attenuation value  $\alpha f^{-2}$  on the concentration are shown for the nitrobenzene–hexane solution at  $T = 294.1$  K and  $f = 5, 15, 50,$  and  $300$  MHz. As is seen from this figure, the value of  $\alpha f^{-2}$  drastically increases at low frequencies and has a maximum at concentrations close to the critical one. When the frequency grows, the amplitude of the maximum diminishes and, at frequencies above 300 MHz, the maximum disappears.

Qualitatively, the same picture is observed for the binary solution nitromethane – *n*-amyl alcohol.

For 5CB liquid crystal, the sound attenuation value is a function of frequency in the range of 2.5–35 MHz and has a maximum at the phase transition temperature  $T_{N-I}$ .

Such a behavior of the sound attenuation factor at low frequencies  $\omega \leq 100$  MHz is connected to the processes of creation and decay of fluctuations of various origins in the systems under investigation, when approaching the CCT of the solution or the phase transition temperature of 5CB liquid crystal [3, 5]. In accordance with the theory of critical phenomena [6–8],

the lifetime of critical fluctuations is determined by the expression

$$\tau_c = \frac{6\pi\eta R_c^3}{k_B T}, \quad (1)$$

where  $\eta = \eta_r(T)(r_0q)^{Z_\eta}t^{-\nu Z_\eta}$  and  $R_c = r_0t^{-\nu}$  are the shear viscosity and the correlation length of the system, respectively. In the neighborhood of  $T_c$ , i.e. at  $t = |T - T_c|/T_c < 10^{-3} - 10^{-4}$ , according to the available experimental data [9–11], the typical lifetime of fluctuations determined by (1) is  $\tau_c \sim 10^{-6} - 10^{-7}$  s. The inverse frequency values  $\omega \approx 10$  MHz ( $\omega^{-1} \approx 10^{-7}$  s), at which a substantial sound attenuation is observed in the studied liquid systems, correspond just to this time interval. At the same time, at frequencies  $\omega \gg 10$  MHz ( $\omega \approx 300$  MHz,  $\omega^{-1} \approx 3 \times 10^{-9}$  s) those values are much less than  $\tau_c$ , and there is no attenuation.

To describe the frequency dependence of the value  $\alpha f^{-2}$ , we used the empirical equation which made allowance for two relaxation times [11]:

$$\frac{\alpha}{f^2} = \frac{A_1}{1 + (\omega\tau_1)^2} + \frac{A_2}{1 + (\omega\tau_2)^2} + B, \quad (2)$$

where  $A_i$  is a low-frequency limit of the value  $\alpha f^{-2}$  in the  $i$ -th region of dispersion ( $\omega\tau_i \ll 1, i = 1, 2$ ),  $B$  is a high-frequency limit of the value  $\alpha f^{-2}$ ,  $\tau_i$  is a relaxation time in the  $i$ -th region of dispersion. The calculation of acoustic spectra was made by an iteration procedure [12]; iterations were continued until the values of unknown quantities that minimized the deviations of  $\alpha f^{-2}$  from experimental ones in the studied frequency interval were found.

The analysis of the temperature dependence of the relaxation frequency in a low-frequency interval (see Fig. 2) showed that, when approaching the critical temperature, the relaxation frequency for nitromethane – *n*-amyl alcohol and nitrobenzene–hexane (at the critical concentration) solutions decreases, which is in agreement with conclusions of the dynamical theory of critical phenomena [3,6].

At low frequencies  $\omega \leq 100$  MHz, investigations of the temperature dependence of the sound attenuation factor  $A_1$  in the systems concerned in the temperature interval  $t \sim 10^{-4} - 10^{-2}$  above CCT were carried out. The results obtained are depicted in Figs. 3 and 4. As is seen from the presented plots, when the temperature approaches  $T_c$  ( $t \rightarrow 0$ ), the value of  $A_1^{-1} \rightarrow 0$ . The data obtained were approximated (see Figs. 3 and 4) by a

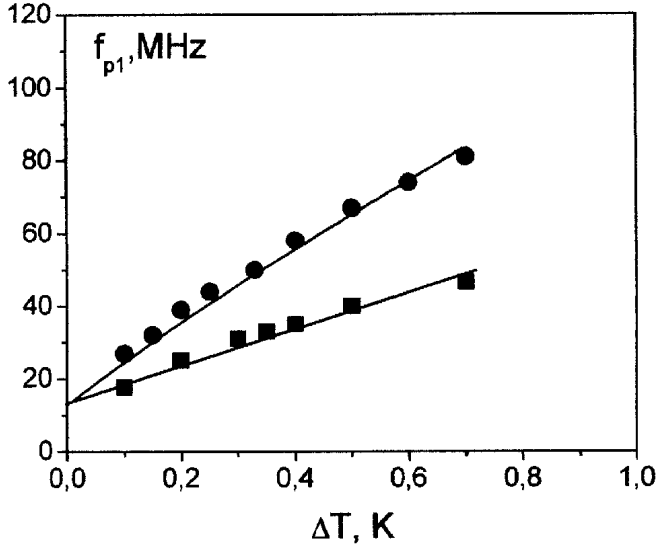


Fig. 2. Dependences of the relaxation frequency in a low-frequency interval of nitrobenzene–hexane (circles) and nitromethane–*n*-amyl alcohol (squares) solutions with critical concentration on the temperature difference  $\Delta T = T - T_c$

power function

$$A_1 = A_{01} t^{-n_1}, \quad (3)$$

where  $A_{01}$  and  $n_1$  are fitting parameters.

Experimental data lead to following values: for nitromethane – *n*-amyl alcohol solution,  $n_1 = 1.1 \pm 0.1$ ,  $A_{01} = 4.6 \times 10^{-16} \text{ m}^{-1}\text{s}^2$ ; for nitrobenzene–hexane solution,  $n_1 = 1.25 \pm 0.02$ ,  $A_{01} = 1.04 \times 10^{-16} \text{ m}^{-1}\text{s}^2$ ; and for 5CB liquid crystal,  $n_1 = 1.1 \pm 0.1$ ,  $A_{01} = 1.85 \times 10^{-13} \text{ m}^{-1}\text{s}^2$  for the isotropic phase and  $n_1 = 1.2 \pm 0.1$ ,  $A_{01} = 3.66 \times 10^{-13} \text{ m}^{-1}\text{s}^2$  for the nematic one.

Thus, the calculations show that the temperature behavior of the sound attenuation factor at low frequencies ( $A_1$ ) is the same for the substances concerned; only the values of the coefficients  $A_{01}$  of the low-frequency attenuation are different. The values, obtained for the power degree  $n_1$  according to (3), are close to results obtained on the basis of a literature data analysis [13,14].

According to the obtained experimental data for  $A_1(t)$  (Figs. 3 and 4) and the temperature dependences of the density  $\rho$  [15,16] and the sound propagation velocity  $c_0$  in the systems concerned, the values of the bulk viscosity  $\eta_{v1}$  were calculated for the low-frequency relaxation interval, making use of formula [4]

$$\eta_{v1} = \frac{A_1 \rho c_0^3}{2\pi^2}, \quad (4)$$

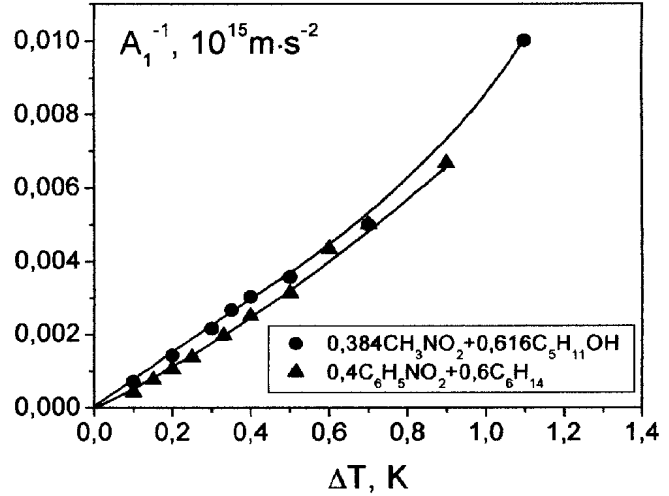


Fig. 3. Dependences of the reciprocal low-frequency sound attenuation on  $\Delta T$  for two binary solutions with critical concentration

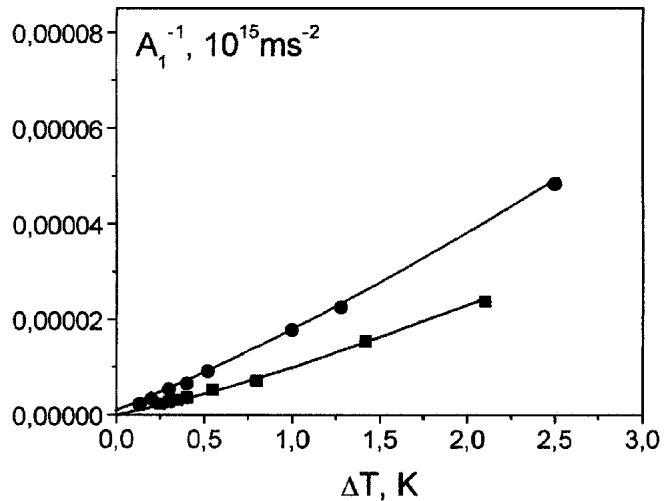


Fig. 4. Dependences of the reciprocal low-frequency sound attenuation on  $\Delta T$  for 5CB liquid crystal (squares correspond to the nematic phase and circles to the isotropic one)

where  $c_0$  is the sound velocity at  $\omega\tau_1 \ll 1$ . The results obtained are shown in Fig. 5 on a log-log scale.

One can see that the obtained dependences  $\eta_{v1}(t)$ , similarly to the dependences  $A_1(t)$  (see Figs. 3 and 4), can be approximated by a power function

$$\eta_{v1} = \eta_{v0} t^{-n}. \quad (5)$$

The fitting parameters  $\eta_{v0}$  and  $n$  for the investigated systems are as follows: for nitromethane – *n*-amyl

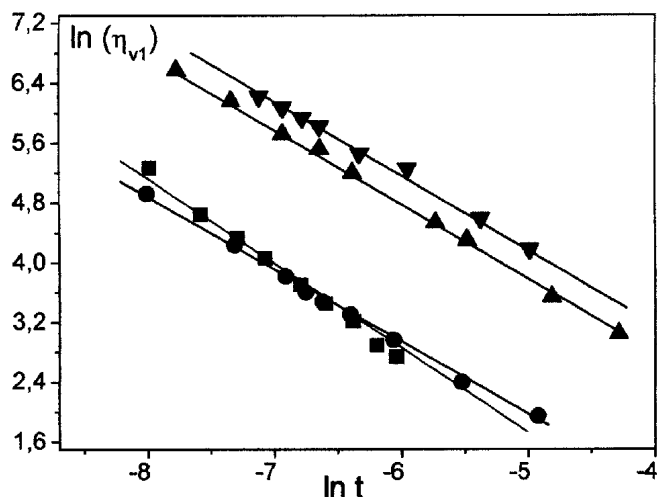


Fig. 5. Dependences  $\eta_{v1}(t)$  on a log-log scale for liquid systems: nitrobenzene-hexane binary solution (squares), nitromethane-n-amyl alcohol binary solution (circles), isotropic (deltas) and nematic (nablas) phases of 5CB liquid crystal

alcohol solution,  $n = 1.1 \pm 0.1$ ,  $\eta_{v0} = 4.55 \times 10^{-2}$  mPa·s; for nitrobenzene-hexane solution,  $n = 1.25 \pm 0.02$ ,  $\eta_{v0} = 8.2 \times 10^{-3}$  mPa·s; and for 5CB liquid crystal,  $n = 1.1 \pm 0.1$ ,  $\eta_{v0} = 30$  mPa·s for the isotropic phase and  $n = 1.2 \pm 0.1$ ,  $\eta_{v0} = 42$  mPa·s for the nematic one.

A comparison of the results obtained for  $\eta_{v1}(t)$  with experimental data for the shear viscosity  $\eta_s(t)$  in the systems concerned evidences for that, in the fluctuation range of temperatures ( $t \sim 10^{-4} - 10^{-2}$ ), the ratio  $\eta_{v1}/\eta_s$  is about a hundred.

The results of studies showed that the temperature behavior of the bulk viscosity is the same for various liquid systems, only the values of the coefficient  $\eta_{v0}$  are different. We believe that this result indicates that if the relaxation mechanism stipulated by the bulk viscosity is considered in the low-frequency interval, one has to make allowance for individual features of solutions.

The investigations performed and the results obtained give a possibility to make the following conclusions. The relaxation region of sound attenuation is observed in the solutions concerned with the critical concentration at frequencies below 300 MHz when approaching CCT. This region results from the creation and decay of critical fluctuations. The fluctuation relaxation time, which characterizes their average lifetime, increases near the critical temperature. The data obtained are in qualitative agreement with the conclusions of the dynamical theory of critical phenomena [6–8].

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#### АКУСТИЧНІ ВЛАСТИВОСТІ РІДИННИХ СИСТЕМ ПОБЛИЗУ КРИТИЧНОЇ ТЕМПЕРАТУРИ

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#### Резюме

Методами акустичної спектроскопії проведено дослідження коефіцієнта поглинання і швидкості поширення звуку в рідинних системах в широкому діапазоні частот, температур і концентрацій, включаючи близький окіл критичної температури розшарування (КТР). Показано, що в досліджуваних розчинах з критичною концентрацією з наближенням до КТР на частотах, нижчих за 300 МГц, спостерігається релаксаційна область поглинання звуку, зумовлена процесами утворення і розпаду критичних флуктуацій. Час релаксації цих флуктуацій, що характеризує середній час їхнього життя, збільшується з наближенням до КТР. Одержані дані якісно узгоджуються з висновками динамічної теорії критичних явищ.