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DETERMINATION OF AVERAGE LENGTHS OF CONCENTRATION WAVES AND OF THE DIFFUSION COEFFICIENT OF THE CRITICAL N-AMYLIC ALCOHOL-NITROMETHANE MIXTURE*

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The kinetics of concentration fluctuations in the critical *n*-amylic alcohol-nitromethane mixture have been analysed in this paper. Average lengths of concentration waves and the diffusion coefficient for investigated mixtures have been established on the basis of results obtained previously by the authors from estimations of the average relaxation time of concentration fluctuations and the radius of their correlation.

1. Introduction

The structure of various liquid mixtures and their molecular micsibility has not been hitherto sufficiently explained. Various methods are being applied in this problem, but optic and acoustic methods prove to be the most useful. The method of molecular light scattering proved very effective in explaining: the state of short-range order in liquids, liquid molecular micsibility and the influence of various factors on the micsibility. Molecular light scattering is caused by non-homogeneities of the dispersion medium. These non-homogeneities in mixtures are: density, concentration and orientation fluctuations of anisotropic molecules.

A strong increase of the absorption of acoustic waves in mixtures in the direct nearness of the critical point, an intensity increase of the central component in the fine structure of Rayleigh light scattering and a strong decrease of

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the diffusion coefficient are all caused by an increase of concentration fluctuations and an increase of its radius of correlation when approaching the critical point.

This paper presents the analysis of the kinetics of concentration fluctuations in an investigated mixture, carried out on the basis of earlier acoustic and optic measurements. Values of the following parameters have been established: average relaxation time of concentration fluctuations, average length of concentration waves, diffusion coefficient.

2. Thermodynamic fluctuations

The fluctuation of an arbitrary thermodynamic quantity is an instantaneous departure of this quantity from its average value. Density and concentration fluctuations in mixtures are important from the point of view of molecular acoustics. For example, in a volume of 10^{-24} m^3 and at a temperature of $T = 20°C$, the density fluctuation for an acetone-nitromethane mixture (concentration $x = 0.5$) is $\delta_\varrho = 1.7\ 10^{-3}$, while the concentration fluctuation is $\delta_x = 1.7 \cdot 10^{-2}$, i.e. 10 times greater. The average value of concentration fluctuations in critical mixtures near the phase transition point, i.e. in the $|T-T_k| \leqslant 1$–$2°$ temperature range, is several hundred times greater than density fluctuations. Therefore, the investigation of properties of critical mixtures can be limited only to concentration fluctuations.

Concentration fluctuations and their characteristic dynamic properties influence the optic and acoustic properties of critical mixtures. According to the thermodynamic theory of fluctuations, the average value of concentration fluctuations in a two-component mixture with the concentration of the components, x_1 and x_2, respectively, is expressed by formula [1]

$$\langle(\Delta x_2)^2\rangle_V = \frac{x_1}{N\left(\dfrac{\partial \ln p_2}{\partial x_2}\right)_{p,T}} \tag{1}$$

where $N = N_1 + N_2$ is the number of particles of the mixture in volume V, p_2 is the partial pressure of the saturated vapour of component "2", i.e. vapour in thermodynamic equilibrium with the mixture. The above formula is valid only for systems in thermodynamic conditions far from critical. It was derived under an assumption that fluctuations in neighbouring volume elements are independent. On the basis of the effect of light scattering near the critical point L. S. ORNSTEIN and F. ZERNIKE [2] as the first assumed that fluctuations in neighbouring volume elements are interdependent, so a correlation between them exists.

Spatial correlation — radial correlation function

If dV_1 and dV_2 denote two small volume elements of a liquid, distant from each other by a distance r, then the probability dW_1 that particle "1" is contained in volume element dV_1 is

$$dW_1 = dV_1/V. \tag{2}$$

Whereas the probability dW_2 that particle "2" is contained in volume element dV_2 is

$$dW_2 = dV_2/V. \tag{3}$$

If positions of particles would be totally independent from each other, then the probability dW_{12} that particle "1" is contained in element dV_1 and particle "2" in element dV_2 would be expressed by formula

$$dW_{12} = \frac{dV_1}{V}\frac{dV_2}{V}. \tag{4}$$

Instead, if we assume that there is a certain correlation between positions of particles, then equation (4) should be written as

$$dW_{12} = g(r)\frac{dV_1}{V}\frac{dV_2}{V}. \tag{5}$$

The function $g(r)$, which describes the correlation, does not depend on the direction of vector $\vec{r}$ and is called the radial function of the distribution of particles. When $r \to \infty$, then $g(r) \to 1$ and edition (5) changes into equation (4).

Because function $g(r)$ is related to probability dW_{12}, it can be considered as the averaged statistic characteristic of the structure of the liquid. The application of the radial distribution function, $g(r)$, allows the determination of the relative frequency of occurrence of various intermolecular distances in the liquid, when the thermodynamic parameters, namely density, temperature and concentration, are given.

The radial distribution function of atoms for simple liquids can be determined on the basis of data obtained from the scattering of X-rays, neutrons or electrons. The relationship between the radial distribution function and distance r usually has a shape as in Fig. 1; r_0 is the radius of the atom. Function $g(r)$ has several maxima and minima; their value tends to 1 with the increase of r. Far from the critical point, function $g(r)$ reaches 1 already for distances equal to 4–5 atom diameters. There is a "long tail" near the critical point, shown at the right side in Fig. 1.

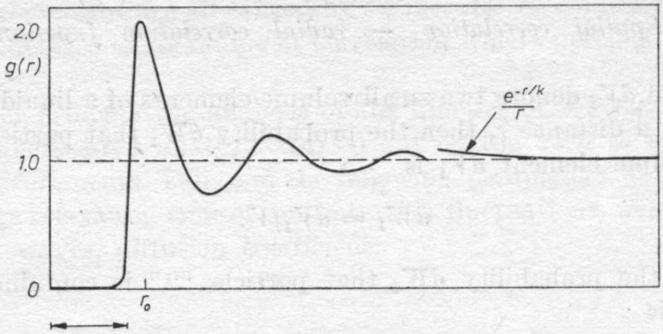

Fig. 1. Radial correlation function for a liquid [3]

Taking advantage of the idea of a correlation between density fluctuations in a liquid in critical conditions, **Ornstein** and **Zernike** [2] derived a formula describing the intensity of scattered light near the critical point (critical opalescence). Due to the existance of the correlation there is an asymmetry of scattering (dependence of the intensity of scattered light on the scattering angle), which can be used in the experimental determination of the radius of density (or concentration) fluctuations correlation [4]. Also on the basis of the above correlation, **Arcovito**, **Faloci**, **Roberti** and **Mistura** [3] proposed a simple explanation of the diffusion effect near the critical point in liquids. According to them, when there is a correlation between density fluctuations with a radius of correlation ξ, then we can imagine that a diffusion process of droplets, which have a radius of the same order as ξ, takes place in the liquid. Of course the atoms "evaporate" and "settle" on the surface of the droplets all the time. In obedience to the Stokes law the mobility of a sphere with a radius ξ is described by expression $(6\pi\eta_s\xi)^{-1}$, while in accordance with Einstein's expression the relationship between mobility and diffusion coefficient has the following form: $D = (k_B t) \times$ (*mobility*). Hence, the diffusion coefficient can be drived from the following expression:

$$D = k_B T / 6\pi\eta_s\xi. \tag{6}$$

Further theoretical considerations, carried out on the basis of the mode coupling theory developed by **Kawasaki** [5], and **Kadanoff** and **Swift** [6], have resulted in an expression for the diffusion coefficient in a hydrodynamic range, which differs from the one presented above only by a constant factor of 1.05.

3. Kinetics of fluctuations

Mixtures with developed concentration fluctuations resemble disperse systems with very small non-homogeneities. They differ from ordinary disperse systems by the fact that concentration fluctuations are unstable. These fluctuations are formed and disappear very quickly. Average lifetimes of concentration fluctuations are inversely proportional to the diffusion coefficient of the mixture. It was experimentally proved [1] that for mixtures with positive departures from the ideal and in thermodynamic conditions distant from critical, relaxation times can be contained in the range 10^{-5}–10^{-11} s. Moving towards the critical point average lifetimes of concentration fluctuations approach infinity.

Kinetics of fluctuations are closely related to the process of propagation of an acoustic wave in critical mixtures. When an acoustic wave propagates in a mixture, the pressure and temperature change periodically. This effect influences the average value of concentration fluctuations and their distribution function, because the average amplitude of concentration fluctuations is p- and T-dependent. The fluctuation distribution attains the equilibrium value with a certain delay, which depends on the diffusion coefficient D.

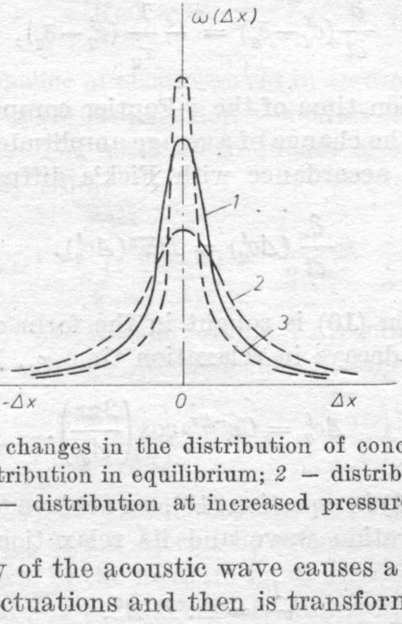

Fig. 2. Example of possible changes in the distribution of concentration fluctuations due to an acoustic wave *1* – distribution in equilibrium; *2* – distribution at reduced pressure; *3* – distribution at increased pressure

A part of the energy of the acoustic wave causes a change in the distribution of concentration fluctuations and then is transformed into heat. The process is irreversible, so acoustic waves are absorbed. When the frequency of acoustic vibrations is sufficiently increased, then the change of the distribution of concentration fluctuations will not occur during one wave period and the fluctuation-induced absorption is not observed. A case in which the distribution function of concentration fluctuations is changed by an acoustic wave is illustrated in Fig. 2.

Let $|\Delta x(r)| = x(r)-\overline{x}$ represent concentration fluctuations. Expanding the distribution of fluctuations into a Fourier series (formal operation introduced by Einstein), we have

$$|\Delta x(r)| = \sum_{q} \overline{c}_q e^{i\vec{q}\,\vec{r}}. \qquad (7)$$

Harmonic components of this spectrum are represented by concentration waves with wave vector $\vec{q}$ and amplitude $\bar{c}_q$. In the state of thermodynamic equilibrium the average amplitude of the Fourier component with wave vector $\vec{q}$, equals

$$\bar{c}_q = f(V, T, x). \tag{8}$$

The distribution function of concentration fluctuations in the field of an acoustic wave differs from the distribution in equlibrium. Therefore, average amplitudes of concentration waves assume new values c_q^t. After the acoustic wave has passed through the mixture, the system will change in the direction of the initial state and $c_q^t \to \bar{c}_q$. According to ONSAGER'S hypothesis it can be accepted that the change of $\bar{c}_q$ in terms of time is subject to the macroscopic law of irreversible processes, so

$$\frac{\partial}{\partial t}(c_q^t - \bar{c}_q) = -\frac{1}{\tau_q}(c_q^t - \bar{c}_q), \tag{9}$$

where τ_q is the relaxation time of the q-Fourier component. Let us assume, as it is usually done, that the change of average amplitudes of concentration waves $\Delta c_q^t = c_q^t - \bar{c}_q$ occurs in accordance with Fick's diffusion equation [7]

$$\frac{\partial}{\partial t}(\Delta c_q^t) = D\nabla^2(\Delta c_q^t). \tag{10}$$

The solution of equation (10) is sought in the form of a concentration wave with length Λ_q, which decays in relaxation time τ_q. Hence we have

$$\Delta c_q^t = Ce^{-t/\tau_q}\cos\left(\frac{2\pi r}{\Lambda_q}\right). \tag{11}$$

Substituting solution (11) in equation (10), we achieve the following relationship between the q-concentration wave and its relaxation time τ_q:

$$\frac{1}{\tau_q} = 4\pi^2 D/\Lambda_q^2. \tag{12}$$

An analogical relationship can be written for a concentration wave, which has an amplitude decaying in relaxation time τ_a. This is the average relaxation time of concentration fluctuations, defined by the following formula [8]:

$$\tau_a = \frac{\int_0^\infty \tau H(\tau)\, d(\ln\tau)}{\int_0^\infty H(\tau)\, d(\ln\tau)} \tag{13}$$

where function $H(\tau)$ is the density of the relaxation time spectrum. $H(\tau)d\tau$ describes the contribution of all Maxwell mechanisms, which have their relaxation times in an interval from τ to $\tau+d\tau$. Function $H(\tau)$ can be determined as the global module per unit interval of the logarithm of relaxation times ($\ln\tau$).

Concentration waves, hitherto considered only as a result of a formal expansion of concentration fluctuations into a Fourier series, correspond to density waves in mixtures; and these – according to MANDELSZTAM [9] – are elastic Debye waves. Taking advantage of this analogy and basing on Debye'a considerations we can estimate the smallest possible length of a concentration wave. If we consider a crystal as a continuum, then its normal vibrations can be determined from the elasticity theory with adequate boundary conditions. The total number of normal vibrations with frequencies contained in an interval from ω to $\omega+d\omega$, is equal to

$$dD(\omega) = \frac{3\omega^2 d\omega}{2\pi^2 v^2} V, \tag{14}$$

where v is the average velocity of elastic waves in an amorphic solid body when $3/v^3 = 2/v_t^3 + 1/v_l^3$; v_t and v_l are propagation velocities of a transverse and longitudinal wave, respectively. The maximal frequency of elastic vibrations can be determined approximately from

$$D(\omega_{\max}) = \int_0^{\omega_{\max}} dD(\omega) = \frac{V\omega_{\max}}{2\pi^2 v^3} = 3N \tag{15}$$

where N is the number of particles in volume V. Assuming that $d^3 = V/Nd$ is the lattice constant or the average intermolecular distance in liquids, we have [9]

$$\omega_{\max} = \frac{2\pi v}{d}\left(\frac{3}{4\pi}\right)^{1/3}, \; \Lambda_{\max} = \left(\frac{4\pi}{3}\right)^{1/3} d. \tag{16}$$

The maximal frequency of elastic Debye waves, $\omega_{\max} = 10^{14}$ Hz, and their minimal wave length, $\Lambda_{\min} = 1.5$ Å, can be estimated from formula (16). All $3N$ elastic waves propagate in the medium in all directions forming a complex, spatial "lattice" of optical non-homogeneities. However, if a parallel light beam, characterized by wave vector k, incides onto such a medium and scattered light is observed in the direction determined by wave vector $\boldsymbol{k}'$, then the maximal intensity of the scattered light will be observed only when wave vectors $\boldsymbol{k}$, $\boldsymbol{k}'$ and $\boldsymbol{q}$ satisfy Bragg's condition [9]. In such a case $|\boldsymbol{q}|$ is described by formula

$$|\vec{q}| = \frac{4\pi n}{\lambda} \sin\frac{\vartheta}{2}. \tag{17}$$

It results from equation (17) that if we use He-Ne laser light with wave length $\lambda = 6328$ Å, then the minimal length of the concentration wave, which can be examined in scattered light will equal approximately 2000 Å (scattering angle equal to 180°). As it will be proved further on, the average length of a concentration wave in critical mixtures will be by 1–2 orders of magnitude shorter.

The Debye approximation of the description of lattice waves [10] assumes that the spectrum of lattice vibrations $D(\omega)$ has a rather specific form. Namely, it is accepted that $D(\omega)$ is proportional to ω^2 near $\omega = 0$, where the material behaves like a continuous elastic medium, and quickly decreases to zero for frequency $\omega_{\max}$. Such a form of function $D(\omega)$ is not justifiable for solids [10], but can considerably well describe the situation in liquids. It has been experimentally and theoretically proved that the spectrum of lattice waves in solids spreads over a considerably wide frequency range and has sharp maxima corresponding to modes with various polarizations and velocities. In low viscosity liquids generally only longitudinal waves occur and they propagate with the same velocity in all directions. Therefore, the spectrum of lattice waves should not exhibit such maxima in liquids. Furthermore, many similarities can be noted between the character of function $D(\omega)$, proposed by Debye, and the distribution function of relaxation times, presented in paper [8]. In this paper we also have a sharp maximum for shorter times and a graduate decrease of the value of the distribution function for longer times.

4. Determination of the average length of a concentration wave in a critical *n*-amylic alcohol-nitromethane mixture

The determination of the spectrum of concentration waves in a series of critical mixtures would supply valuable information concerning the kinetics of concentration fluctuations and widen the knowledge of such phenomena and effects as light scattering or propagation of acoustic waves in such media. Yet this is a rather complex problem for solids and a very complex one for liquids with their random character of particle motion. Most formulations of the spectrum of concentration waves in liquid media have the character of qualitative predictions rather than exact empirical or theoretical solutions.

On the basis of the above mentioned analogy between concentration waves and, density and elastic Debye waves, it can be found that the determination of the spectrum of concentration waves is tantamount to the determination of the spectrum of normal vibrations. In a solid body the problem is reduced to the solution of the following system of 3 N equations [10]:

$$\sum_{s'j'} \{G_{ss'}^{jj'}(q) - \omega^2 M_s \delta_{ss'} \delta_{jj'}\} U_{sq}^{j'} = 0 \tag{18}$$

where $U_{s,q}$ are lattice deflections with a time factor $\exp(i\omega t)$; $G_{s,s'}(q)$ is the tensor describing interatomic interactions; M_s is the mass of the s-atom. The solution of these equations for a dense network of wave vectors $\boldsymbol{q}$ gives values ω_q

from every interval $d\omega_q$. As it has been mentioned previously the situation is more complex in liquids, which are random media, and the determination of the distribution of Debye waves is still to be done. Of course the determination of the average length of concentration waves is not tantamount to the determination of the spectrum of these waves. Yet all the same it leads to several inferences concerning the behaviour of such a spectrum in terms of temperature and concentration of the mixture.

In order to establish the average length of concentration waves according to formula (12) we have to know the average relaxation time of concentration fluctuations and the diffusion constant of the mixture. Relaxation times, τ_a, in the critical *n*-amylic alcohol-nitromethane mixture have been determined with the application of the method described in papers [8, 11] for various concentrations and for two temperatures. Values of diffusion coefficients for these temperatures and concentrations have been calculated from formula (6). The radius of correlation, ξ for this mixture has been determined by the authors previously with the utilization of the effect of Rayleigh light scattering [4, 12]. Values of the radius of correlation for chosen concentrations and temperatures were calculated from [13]:

$$\xi = \xi_1[|T-T_k|+d(x-x_k)^3]^{-0.6}. \tag{19}$$

Final calculation results are presented in Table 1.

Table 1

Concentration of n-$C_5H_{11}OH$ [mole fraction]	T [K]	ξ [10^{-10} m]	$D\cdot10^3$ [$m^2\,s^{-1}$]	Λ_a [10^{-2}m]	τ_a [s]
0.1	302.35	6.1	39.2	$2.5\cdot10^{-6}$	$4.05\cdot10^{-10}$
	313.15	4.0	74.3	$3.8\cdot10^{-6}$	$5.03\cdot10^{-10}$
0.3	302.35	18.5	7.4	$1.1\cdot10^{-5}$	$4.04\cdot10^{-8}$
	313.15	5.5	31.2	$6.7\cdot10^{-6}$	$3.60\cdot10^{-9}$
0.385	302.35	20.4	5.7	$2.2\cdot10^{-5}$	$2.23\cdot10^{-7}$
	313.15	5.6	26.3	$4.4\cdot10^{-6}$	$1.91\cdot10^{-9}$
0.5	302.35	16.4	5.9	$9.6\cdot10^{-6}$	$3.99\cdot10^{-8}$
	313.15	5.4	22.9	$3.4\cdot10^{-6}$	$1.34\cdot10^{-9}$

Figs. 3 and 4 illustrate D and τ_a in terms of concentration in a critical *n*-amylic alcohol-nitromethane mixture for two temperatures: 29.2 and 40°C. In accordance to the theory, the average relaxation time of concentration fluctuations increases when approaching the critical point, while the diffusion coefficient decreases. Figs. 5 and 6 present the relationship between the average length of concentration waves and the concentration of the mixture for the same

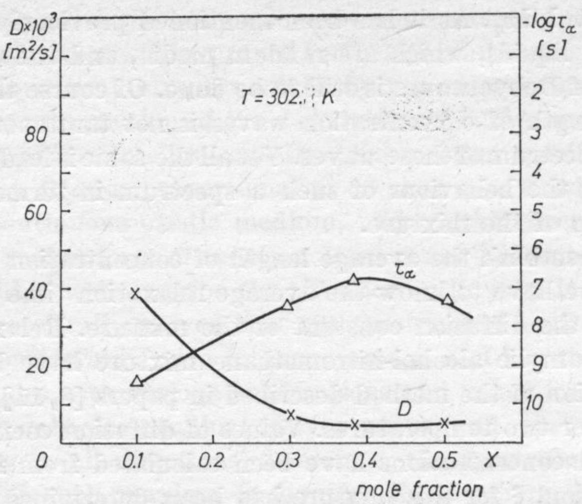

Fig. 3. D and τ_a in terms of concentration in the critical n-amylic alcohol-nitromethane mixture at temperature $T = 302.35$ K

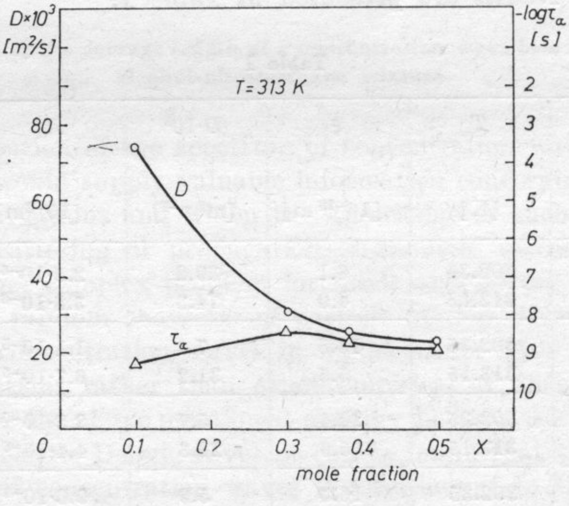

Fig. 4. D and τ_a in terms of concentration in the critical n-amylic alcohol-nitromethane mixture at temperature $T = 313.15$ K

two temperatures. As it can be seen, the average length of concentration waves increases by one order of magnitude, when conditions of the mixture approach critical conditions. This indicates that the spectrum of concentration waves moves towards lower frequencies.

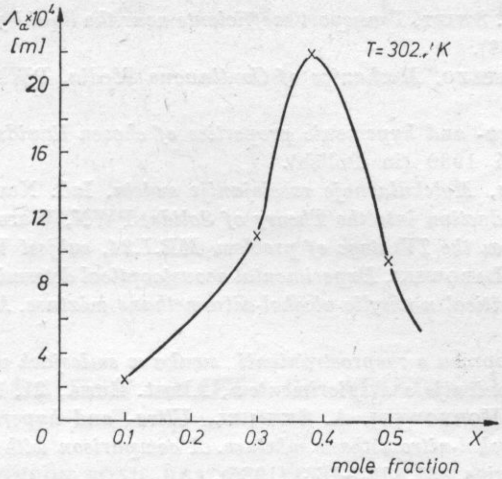

Fig. 5. The average length of concentration waves in terms of concentration in the critical n-amylic alcohol-nitromethane mixture at temperature $T = 302.35$ K

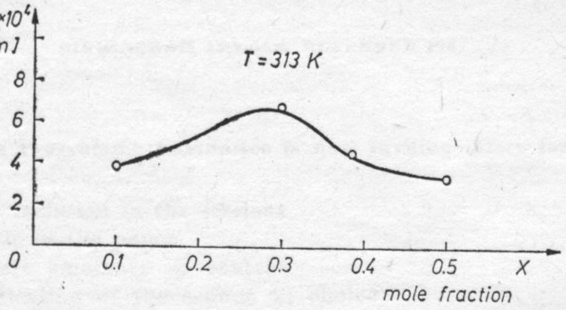

Fig. 6. The average length of concentration waves in terms of concentration in the critical n-amylic alcohol-nitromethane mixture at temperature $T = 313.15$ K

References

[1] M. I. Szachparonow, *Wwiedienije w sowriemiennuju tieoriju rastworow*, Izd. "Wysszaja Szkoła", 1976.

[2] M. A. Leontowicz, *Statistic Physics*, PWN, Warszawa 1957 (in Polish).

[3] H. L. Swinney, *Kriticzeskije jawlenije w żidkostjach*, in: Spiektroskopija opticzeskogo smieszenija i korrielacja fotonow, ed. H. Z. Cumnins and E. R. Pike, Izd. Mir, Moskwa 1978.

[4] T. Hornowski, M. Łabowski, *Experimental determination of the radius of correlation of concentration fluctuations in the critical n-amylic alcohol-nitromethane mixture*, Proc. XXXII OSA, 179-182, Kraków 1985 (in Polish).

[5] K. Kawasaki, *Sound attenuation and dispersion near the liquid-gas critical point*, Phys. Rev., 1A, 1750 (1970).

[6] L. P. Kadanoff, J. Swift, *Transport coefficients near the liquid-gas critical point*, Phys. Rev., 166, 89 (1968).

[7] L. Landau, E. Lifszyc, *Mechanics of Continuous Media*, PWN, Warszawa 1958 (in Polish).

[8] M. Łabowski, *Ultra- and hypersonic properties of chosen liquids and critical mixtures*, Ed. UAM, Poznań 1980 (in Polish).

[9] I. L. Fabielinskij, *Molekularnoje rassiejanije swieta*, Izd. Nauka, Moskwa 1965.

[10] J. M. Ziman, *Introduction into the Theory of Solids*, PWN, Warszawa 1977 (in Polish).

[11] *Scientific report from the IV stage of problem MR.I.24, subject VI.4* (in Polish).

[12] T. Hornowski, M. Łabowski, *Experimental acoustooptical determination of some physical parameters of the critical n-amylic alcohol-nitromethane mixture*, Acta Physica Polonica, A69/4 (in print).

[13] I. A. Czaban, *K woprosu o rasprostranienii zwuka w smiesjach wblizi kriticzeskoj toczki rassłaiwanija. Srawnienije s ekspierimentom*, Akust. Żurn., **21**, 1, 286–293 (1975).

[14] M. Łabowski, T. Hornowski, A. Skumiel, *Ultra- and hypersonic properties of the critical n-amylic alcohol-nitromethane mixture. A comparison with the theories of Fixman and Chaban*, Acustica, **57**, 175–184 (1985).

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