Universality of critical dynamics of nematic liquid crystals

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(Submitted 5 June 1984)
Zh. Eksp. Teor. Fiz. **87**, 1969–1983 (December 1984)

An investigation was made of acoustic relaxation in MBBA and BMOAB liquid crystals in the isotropic and nematic phases. A universal dependence of the absorption and of the velocity dispersion of sound on the reduced frequency $\omega\tau$ (τ is the characteristic relaxation time) was observed in the range $\omega\tau = 10^{-2}$–10^2. Selection of the relaxation time (instead of temperature) as a scaling factor made it possible to match quantitatively the anomalies of equilibrium and dynamic properties.

1. INTRODUCTION

The nature of the critical phenomena that occur near the nematic-isotropic liquid (*NI*) phase transition is not yet clear, in spite of the apparent simplicity of this transition and numerous investigations (for a review see, for example, Ref. 1). The results of recent experimental investigations of the specific heat,[2] order parameter,[3] and susceptibility[4] have demonstrated once again the difficulties encountered when the *NI* transition is described in the traditional way using the Landau–de Gennes expansion.[5] An alternative approach has not yet been developed because no reliable information is available on the true nature of the asymptotic laws (critical exponents). Moreover, it has not yet been possible to match the behavior of various equilibrium dynamic properties near the *NI* transition, so that an acceptable phenomenological model is not yet available. For example, the specific heat in the nematic phase can be described by the Landau–de Gennes expansion including terms of the sixth order and also fluctuation corrections. However, a satisfactory description of the temperature dependence of the order parameter requires different values of the expansion coefficients. In any case, the fourth-order term is anomalously small, so that subject to certain qualifications we can speak of "tricritical" nature of the *NI* transition.[2] Unfortunately, the tricritical hypothesis makes it difficult to obtain agreement between the specific heat and susceptibility in the isotropic phase. The main reason for these difficulties is that the *NI* transition is of the first order and the approach to temperature of divergence of the susceptibility (T^*) is limited to the interval

$$t=\frac{|T-T^*|}{T^*}>\frac{|T^*-T_{NI}|}{T_{NI}}>10^{-3},$$

where T_{NI} is the temperature of the *NI* transition. Experimentalists therefore have to determine the nature of the asymptotic laws within just one order of variation of t. Moreover, there are no grounds for assuming that these will be simple power laws linked by universal relationships, as in the vicinity of a second-order phase transition. We can use the following analogy with the critical point of the liquid-gas transition. If the density of the sample differs from the critical value, the transition is of the first order. In this case the temperature dependences of the physical quantities cannot be described by simple power laws (critical exponents cannot be deduced from them). Nevertheless, it is possible to retain a universal description if instead of temperature we use the susceptibility or specific heat as the scaling factor (for a review see Ref. 6). In the case of dynamic properties a natural scaling factor is the relaxation time τ and the second variable linked to this factor is the frequency ω.

We carried out an experimental study with the aim of determining the nature of the critical dynamics near the *NI* transition without making any *a priori* assumptions about the nature of the anomalies of the equilibrium properties and not using T^* as a fitting parameter. With this in mind we posed the following questions.

1. Do there exist homogeneous functions of variables ω and τ describing acoustic relaxation in the isotropic and nematic phases?

2. Are these functions universal and what is their form?

3. What are the requirements that are imposed on the critical anomalies of equilibrium properties by the universality and asymptotic ($\omega\tau \ll 1$ and $\omega\tau \gg 1$) behavior of the dynamics?

The answers can be summarized as follows.

The critical dynamics of the isotropic and nematic phases of the two investigated substances (MBBA and BMOAB) is governed wholly by the actual characteristic relaxation time, which is in one-to-one relationship with the susceptibility. The anomalous parts of the absorption and dispersion are described by homogeneous universal functions. The explicit form of these functions for the isotropic phase is similar to that in the model of Imura and Okano.[7] Retention of the homogeneities by the functions for the nematic phase imposes serious restrictions on the relationship between the fluctuation mechanism of acoustic relaxation and the contribution of the relaxation of the order parameter. Selection of the relaxation time as the scaling factor instead of $T - T^*$ makes it possible to match, within the scaling framework, the equilibrium and dynamic properties near the *NI* transition.

2. EXPERIMENTAL INVESTIGATION

We carried out a detailed study of the temperature dependence of the absorption coefficient and of the dispersion

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of the phase velocity of sound in the isotropic and nematic phases of unoriented samples of two liquid crystals: MBBA (4-methoxybenzylidene-4′-n-butylaniline) and BMOAB (4-n-butyl-4′-methoxyazoxybenzene). In the case of MBBA there are extensive experimental data on various properties, including the temperature dependence of the viscosity[8] and of the line width of scattered light,[9] as well as on acoustic relaxation.[10,11] The second liquid crystal (BMOAB) is characterized by a high chemical stability and a low concentration of impurities.[1)] The most important point is that precision data on the specific heat were obtained earlier for our samples.[2] Previously evacuated cells were filled with liquid crystals in an atmosphere of an inert gas (helium or nitrogen).

A cell with a sample was a stainless-steel cylinder in an isothermal copper can. The volume of the cell was $\sim 70\ \text{cm}^3$. A source and a detector of sound, both made of X-cut quartz plates (disks 20 mm in diameter), were attached to acoustic guides with a total length 115 mm and also made of stainless-steel. A rod was used to displace the upper mobile acoustic guide with the source by a distance of up to 20 mm relative to the lower one. The acoustic base length was measured in the clockwise direction.

A thermometric bridge and a heater both connected to a temperature stabilization system were placed on the isothermal can surrounding the cell. The cell was also surrounded by a copper screen the temperature of which followed automatically the temperature of the cell. The transfer of heat to the cell was minimized by ensuring that the leads and the acoustic guide drive rod were in thermal contact with a copper block the temperature of which was kept equal to the cell temperature; the whole enclosure was evacuated. Temperature was measured with a platinum resistance thermometer. The thermostatting error did not exceed 3 mK during one measurement. The details of the apparatus were described earlier.[12]

The main distorting factors near the phase transition were the temperature gradients and the nonequilibrium state of a sample.[6] We stirred a liquid crystal to eliminate inhomogeneities and to reduce the time taken to reach equilibrium. The stirring was performed by repeated rapid motion of the mobile acoustic guide. The temperature gradients did not exceed 0.5 mK/cm. The time taken to establish equilibrium in a sample after a change in temperature did not exceed 1 h.

The temperature dependences of the phase velocity and of the absorption coefficient of ultrasound were determined at frequencies in the range 0.9–26.5 MHz at temperatures from 20 to 100 °C. This range of frequencies and temperatures made it possible to vary the product $\omega\tau$ by four orders of magnitude.

The velocity of sound was measured by a phase-pulse method. An amplified rf pulse crossed the investigated substance and interfered with a reference signal oscillating at the carrier frequency. The error in the determination of the phase velocity did not exceed 0.15%. The absorption coefficient of sound was deduced from the change in the amplitude of an rf pulse which traveled a known distance. The error in the absorption measurements was 1–5%, with the exception of the frequency 0.9 MHz at which the scatter of the results far from the transition point (where the absorption was weak) increased to 20% as a systematic error appeared; in the calculation of the excess absorption we regarded this error as the fitting parameter and included it in the regular part. Measurements of the absorption coefficient and velocity of sound were carried out simultaneously. The results obtained for MBBA were in qualitative agreement with the published data.[10] The transition temperature T_{NI} was taken to be the value corresponding to an abrupt change in the absorption coefficient and in the velocity of sound in a sample. Our prolonged investigation involving repeated heating and cooling reduced the value of T_{NI} by 0.3–0.5 K in the case of MBBA and by 0.05–0.1 K in the case of BMOAB. An objective analysis of the results belonging to different series and a comparison with the published data on acoustic and other properties required selection of a consistent temperature scale. It was natural to select $T - T_{NI}$ as the scale for all the anomalous properties and the absolute temperature T for the quantities which changed only slightly in the vicinity of the transition point, such as viscosity, regular part of the velocity of sound, etc.

The excess absorption coefficient α' was deduced from the experimental data by subtracting the regular part associated with the shear viscosity (η) and the noncritical part of the volume viscosity (η_V):

$$\frac{\alpha'}{\omega^2}=\frac{\alpha}{\omega^2}-\frac{2\pi^2}{\rho v^3}\left(\frac{4}{3}\eta+\eta_V\right), \tag{1}$$

where v is the velocity of sound and ρ is the density of the crystal. The values of the shear viscosity for the isotropic phase of MBBA (Ref. 8) were approximated by the dependence $\eta(T) = 0.594\times10^{-6}\exp(4040/T)$ P and the value of the noncritical part η_V was employed as the fitting parameter. The criterion of validity of any theoretical model is the condition $(\alpha'\lambda)\sim\omega\tau$ (λ is the wavelength of sound) in the hydrodynamic range ($\omega\tau\ll1$). In view of the absence of data on the viscosity of BMOAB, the regular part of the absorption in this substance was determined entirely from the criterion given above and was found to be close to the value for MBBA. The experimental dependences of the absorption coefficient and of the velocity of sound on the frequency and temperature can be seen in Figs. 1 and 2.

The homogeneity of the dispersion of the velocity of sound and of the anomalous part of the absorption coefficient (considered as functions of the frequency and temperature) indicates that

$$1-(v/v_\infty)^2=A(T)\varphi_1(\omega\tau), \tag{2}$$

$$\alpha'\lambda=\pi A(T)\varphi_2(\omega\tau), \tag{3}$$

where v_∞ is the velocity of sound[2)] extrapolated to the limit $\omega\to\infty$ from the critical relaxation region (it is represented by a regular function which is not affected by the proximity to T_{NI}); φ_1 and φ_2 are functions of the reduced frequency $\omega\tau(T)$; $A(T)$ depends only on temperature. If the homogeneity does indeed exist then the excess absorption and the dispersion can be represented in the form

$$\begin{aligned}\lg\,(1-v^2/v_\infty{}^2)&=a_n+\tilde\varphi_1(\lg\omega+b_n),\\ \lg\,(\alpha'\lambda/\pi)&=a_n+\tilde\varphi_2(\lg\omega+b_n),\end{aligned} \tag{4}$$

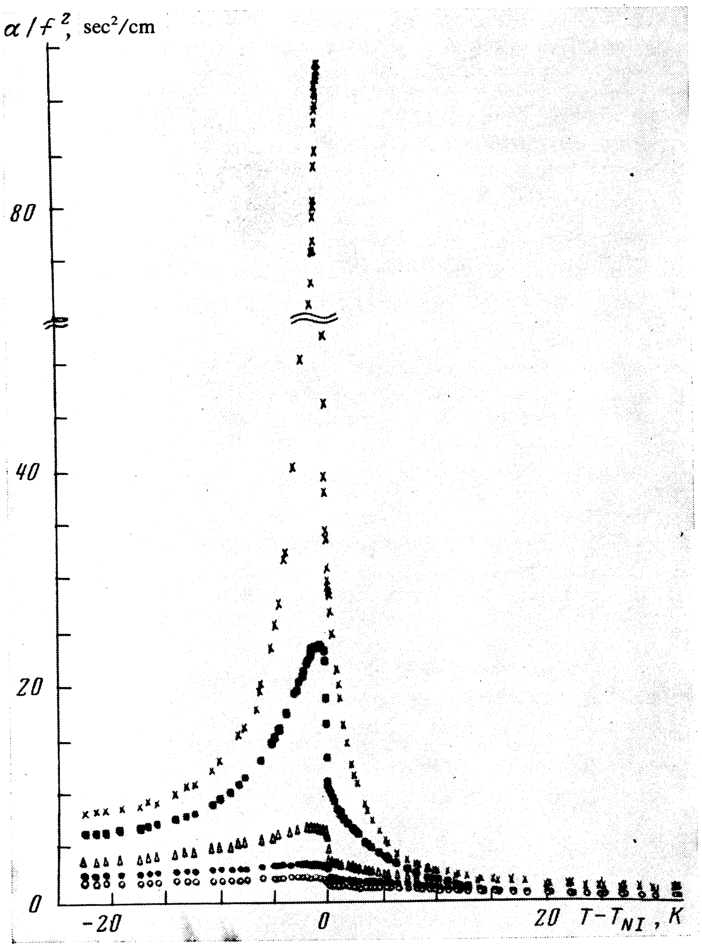

FIG. 1. Absorption coefficient of sound divided by the square of the frequency (in units of 10^{17}) recorded near the *NI* transition in MBBA ($f=\omega/2\pi$ and $T_{NI} = 314.913$ K): ×) 1.5 MHz; ■) 3.8 MHz; △) 9.4 MHz, ●) 15.1 MHz; ○) 20.9 MHz.

where $a_n = \log A(T_n)$; $b_n = \log\tau(T_n)$; n is the number which labels an experimental point. Then a series of experimental curves, such as the dependences of $\log(\alpha'\lambda)$ on $\log\omega$ (Fig. 3), should reduce to the same dependence $\tilde{\varphi}_1 = \log\varphi_1$ (or $\tilde{\varphi}_2 = \log\varphi_2$) if the individual curves are displaced by an amount a_n along the $\log(\alpha'\lambda)$ axis and by b_n along the $\log\omega$ axis. Such a procedure was carried out for both phases of MBBA and MBOAB. The additional fitting parameter in the analysis of the dispersion was the quantity v_∞ (Fig. 1). It was found that in all cases the dispersion and the excess absorption were (within the limits of the experimental error) homogeneous functions of the temperature and frequency.

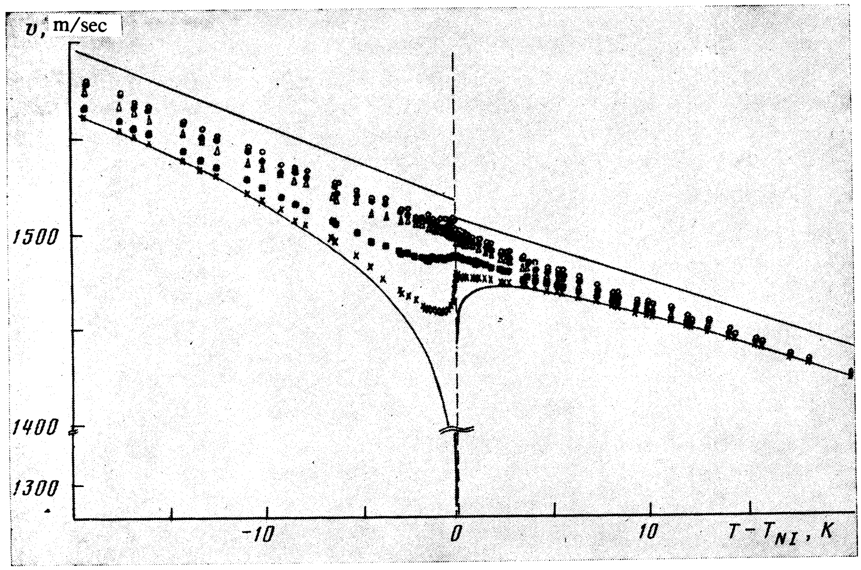

FIG. 2. Velocity of sound near the *NI* transition in MBBA (notation as in Fig. 1). The lower and upper continuous curves represent the temperature dependences of $v(\omega \to 0)$ and v_∞. The discontinuity of v_∞ at the transition point is due to a density discontinuity,

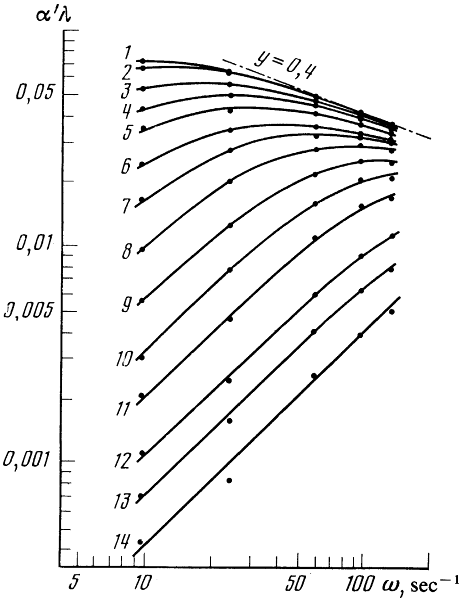

FIG. 3. Excess absorption per unit wavelength in the isotropic phase of MBBA, plotted for the following reduced temperatures $T - T_{NI}$: 1) 0.019; 2) 0.092; 3) 0.601; 4) 1.066; 4) 1.066; 5) 1.493; 6) 2.467; 7) 3.580; 8) 5.383; 9) 8.179; 10) 11.585; 11) 15.373; 12) 21.953; 13) 26.604; 14) 32.839.

However, these functions were identical for the two substances, but different for the isotropic and nematic phases (Figs. 4 and 5).

We can thus see that a search for the homogeneity yielded the relaxation times at each temperature, the functions $A(T)$ (they were indeed found to be the same for the velocity dispersion and the absorption of sound), and the functions $\varphi_1(\omega\tau)$ and $\varphi_2(\omega\tau)$. It should be stressed that the existence of homogeneous functions of the (2) and (3) type automatically means that there is one (and only one) time scale,[3)] which is the temperature-dependent relaxation time τ.

3. DISCUSSION OF EXPERIMENTAL RESULTS. LANDAU THEORY OR SCALING?

The dispersion of the velocity and of the absorption of sound are governed respectively by the real and imaginary parts of the complex adiabatic compressibility $\tilde\beta_S$ which are frequency-dependent:

$$\tilde v^2 = v_\infty^2 - \Delta\tilde v^2, \tag{5}$$

where

$$\tilde v^2 = (\rho\tilde\beta_S)^{-1}, \quad \mathrm{Re}\,\tilde\beta_S^{-1} = \beta_S^{-1} = \rho(\partial P/\partial\rho)_S$$

(P is the pressure and S is the entropy); $\Delta\tilde v^2(\omega,\tau)$ is a complex quantity describing the critical absorption and the critical dispersion:

$$\mathrm{Im}(\Delta\tilde v^2/v_\infty^2) = \alpha'\lambda/\pi, \quad \mathrm{Re}(\Delta\tilde v^2/v_\infty^2) = 1-(v/v_\infty)^2.$$

The critical absorption and dispersion in the nematic phase are governed by at least two mechanisms: relaxation of the order parameter (Q_{ij}) and relaxation of the correlation function of fluctuations of the order parameter ($\langle Q_{ij}Q_{ji}\rangle$). In the isotropic phase the fluctuation mechanism is the only one acting. The existence of two mechanisms of the critical relaxation makes it possible to answer, in principle, the following question by an experimental study: do the fluctuations reduce to just small corrections (Landau theory) or are they so large that they determine the nature of the effect (scaling)?

A. Self-consistent field approximation (Landau theory)

In this approximation the complex adiabatic compressibility can be found by expanding the pressure and entropy as a series in terms of the order parameter (up to quadratic terms inclusive) and in terms of the equilibrium temperature (see, for example, Ref. 13). Substituting in these expansions the values of the order parameter and of the correlation function found from the relaxation equations,[14] we obtain

$$\Delta\tilde v^2(\omega,\tau) = A_1(T)F_1(x) + A_2(T)F_2(x), \tag{6}$$

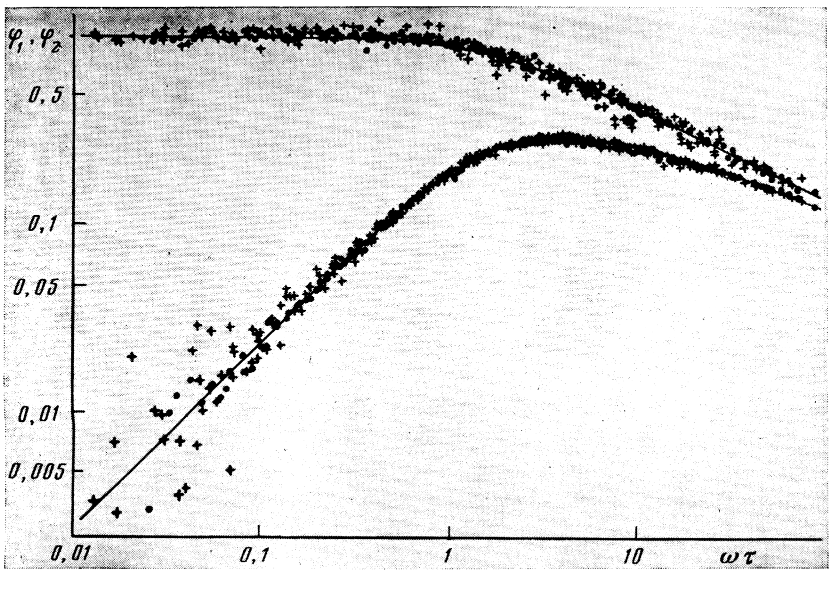

FIG. 4. Universal functions φ_1 and φ_2 for the isotropic phase of MBBA (●) and BMOAB (+). The continuous curves represent the Imura-Okano functions [Eq. (29)].

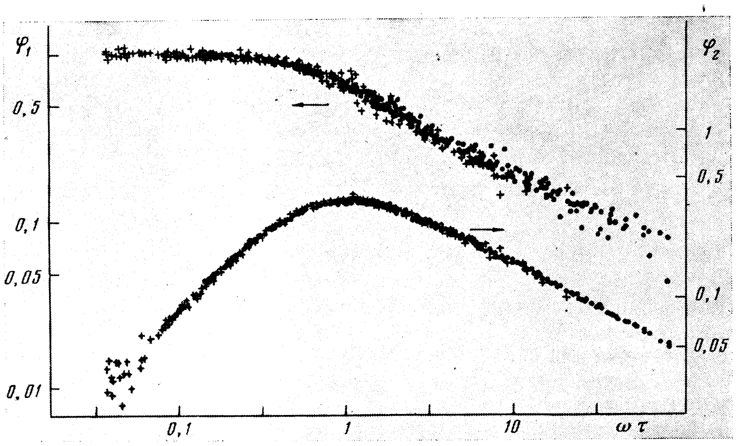

FIG. 5. Universal functions φ_1 and φ_2 for the nematic phase of MBBA (●) and BMOAB (+). The scales for φ_1 and φ_2 are shifted relative to one another to avoid crossing.

where $x = i\omega\tau$,

$$F_1(x)=(1+x)^{-1}, \tag{7}$$

$$F_2(x)=(x/2)^{-1/2}[(2/x-1)^{1/2}-(2/x)^{1/2}]. \tag{8}$$

Here $A_1(T)$ and $A_2(T)$ are real functions of temperature:

$$A_1(T)=(\partial P/\partial Q)_{S,\rho}(\partial Q/\partial\rho)_S, \tag{9}$$

$$A_2(T)=\left(\frac{\partial^2 P}{\partial Q^2}\right)_{S,\rho}\left(\frac{\partial\chi^{-1}}{\partial\rho}\right)_S\frac{V_m(\chi^{-1}b^3)^{-1/2}}{32\pi} \tag{10}$$

(V_m is the volume per one molecule; in the case of MBBA, this volume is $V_m \approx 470$ Å^3).

The quantities occurring in Eqs. (9) and (10) can be found by expanding the molar thermodynamic potential $\Phi(T, P, Q)$ in terms of the modulus of the order parameter:

$$\Delta\Phi/RT_{NI}={}^1/_2 atQ^2+{}^1/_3 BQ^3+{}^1/_4 CQ^4+{}^1/_5 DQ^5+{}^1/_6 EQ^6+{}^1/_2 b(\nabla Q)^2 \tag{11}$$

(R is the universal gas constant). In this approximation the reciprocal susceptibility is

$$\chi^{-1}=\left[\frac{\partial^2}{\partial Q^2}\left(\frac{\Delta\Phi}{RT_{NI}}\right)\right]_{P,T}$$

and the correlation length is $r_C = (b\chi)^{1/2}$. The correlation length for the isotropic phase is $r_C = (b/at)^{1/2} = r_0 t^{-1/2}$. The expansion (11) is obtained ignoring biaxial and transverse fluctuations of the tensor Q_{ij} which clearly do not contribute significantly to the critical absorption and dispersion.

We shall now give approximate (to within one constant factor g) estimates of A_1 and A_2 which can be used to carry out direct calculations with the aid of the expansion given by Eq. (11):

$$A_1(T)=\frac{\partial Q}{\partial T}\left[\frac{\partial}{\partial T}\left(\frac{\partial\Phi}{\partial Q}\right)\right], \tag{12}$$

$$A_2(T)=g\left[\frac{\partial}{\partial T}(\chi^{-1})\right]^2\frac{RTV_m(\chi^{-1}b^3)^{-1/2}}{32\pi}. \tag{13}$$

The first term in Eq. (6) is related to relaxation of the order parameter (Landau-Khalatnikov mechanism[15]), whereas the second is associated with relaxation of the correlation function (Ornstein-Zernike approximation) and is proportional to the fluctuation part of the molar specific heat:

$$\Delta C_p=\frac{nRT^2V_m}{16\pi}\left(\frac{\partial\chi^{-1}}{\partial T}\right)^2(\chi^{-1}b^3)^{-1/2}, \tag{14}$$

where n is the number of fluctuating components of the order parameter. For the nematic phase we can assume that $n = 1$, which corresponds to an allowance for just the longitudinal fluctuations. In the isotropic phase, considered in the approximation of one correlation length, we find that $n = 5$. The condition of homogeneity [Eqs. (2) and (3)] can be satisfied only if the temperature dependences of A_1 and A_2 are the same. We can easily see that the form of the functions A_1 and A_2 is governed by the ratio of the constants of the expansion (11) and the same temperature dependence can be obtained only for a special selection of the constants (for example, if $B = C = D = 0$). We shall try to match the acoustic data with the specific heat of the nematic phase of MBBA using the following set of the expansion coefficients in Eq. (11): $a = 1.4$, $B = -0.06$, $c = 0.1$, $D = 0$, $E = 0.33$, and $b/a = r_0^2 = 36$ Å^2, which makes it possible to describe satisfactorily the temperature dependences of the specific heat, as well as the discontinuities of the entropy [$(\Delta S/R) \approx 0.1$ - Ref. 2] and of the order parameter ($\Delta Q \approx 0.3$ - Refs. 3 and 16). The temperature dependence of the order parameter is described less satisfactorily, but the experimental data of different authors[3,16] differ greatly. We can see from Fig. 6 that the departure from homogeneity is slight and, generally, it is of the same order as the error in the description of the equilibrium properties [corresponding to a different set of the coefficients of the expansion in Eq. (11) for BMOAB—see Ref. 4]. Nevertheless, it is not very likely that the homogeneity found experimentally for the two samples, which is indeed a universal property of the NI transition, is the result of a random (and fairly fine) interplay of constants. Moreover, it is worth noting the large value of the fluctuation contribution to the properties of the nematic phase: A_2/A_1 varies from 0.2 for $T_{NI} - T = 15$ K to 0.33 for $T_{NI} - T = 0.1$ K. At high frequencies the fluctuation mechanism is practically the only one, because

$$\lim_{x\to\infty} F_1(x) \sim x^{-1}, \quad \text{and} \quad \lim_{x\to\infty} F_2(x) \sim x^{-1/2}.$$

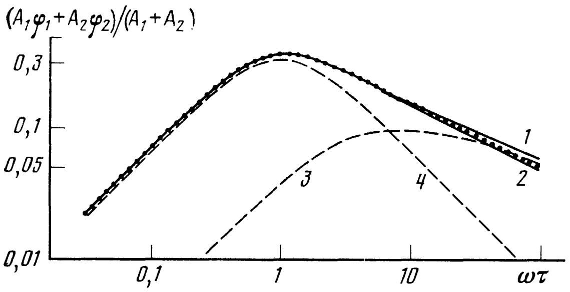

FIG. 6. Results of a calculation of the absorption coefficient of the nematic phase of MBBA, carried out in the self-consistent field approximation using Eqs. (6)-(8), (12), and (13) (here, $\varphi_1 = \mathrm{Im}F_1, \varphi_2 = \mathrm{Im}F_2$): 1) $T_{NI} - T = 0.1$ K; 2) $T_{NI} - T = 1.0$ K; 3) $A_2 \cdot \mathrm{Im}F_2$ (for $T_{NI} - T = 0.1$ K); 4) $A_1 \cdot \mathrm{Im}F_1$ (for $T_{NI} - T = 0.1$ K). The points are the experimental values.

In the case of the isotropic phase, for which the pretransition effects are entirely due to fluctuations, the experimental temperature dependence of the specific heat is not described by Eq. (14) and in the case of the susceptibility we need to include the fluctuation corrections that go beyond the Ornstein-Zernike approximation (see Ref. 4).

It is possible that by including the higher orders of perturbation theory and varying the resultant additional fitting parameters we may finally be able to match the existing experimental data. However, this approach seems artificial to us and in conflict with the very essence of the Landau theory.

We shall estimate the Ginzburg criterion (see Ref. 14) representing the range of validity of the self-consistent field approximation ($t \gg \mathrm{Gi}$) by using the constants given above. Comparing the specific heat discontinuity ($a^2/2C$), obtained from the expansion (11) ignoring the cubic term, with the fluctuation part of the specific heat [Eq. (14)], we find the following expression for the isotropic phase:

$$\mathrm{Gi} = \frac{n^2}{64\pi^2}\frac{V_m^2}{r_0^6}\frac{C^2}{a^4} \sim 10^{-3}.$$

Since $(V_m^{1/3}/r_0) \gtrsim 1$ (intermolecular short-range interaction), the smallness of Gi is governed by the anomalously small constant $C \approx 0.1$ (tricritical behavior). This estimate shows that the limit of validity of the Landau theory ($t \sim \mathrm{Gi}$) is in any case close (in respect of the order of magnitude) to the transition temperature. Therefore, near T_{NI} we can expect crossover (from the average-field to the fluctuation case) behavior of the physical properties.

B. Scaling

Dynamic scaling describes the universal dynamics of systems with highly developed fluctuations. The critical part of the complex adiabatic compressibility is then a homogeneous function of temperature (see, for example, Ref. 17),

$$\Delta\tilde{v}^2/v_\infty{}^2 = \tau^y \psi(x), \tag{15}$$

where $y = \alpha/z$; α and z are, respectively, the critical exponents of the specific heat ($\Delta C_P \propto t^{-\alpha}$) and of the relaxation time ($\tau \propto t^{-z}$). We shall find the dispersion and absorption of sound in the hydrodynamic range ($x \ll 1$), where $\psi(x)$ is an analytic function

$$\psi(x) = \psi(0) + \psi'(0)x + {}^1\!/_2\psi''(0)x^2 + \dots, \tag{16}$$

$$\frac{v_\infty{}^2 - v^2}{v_\infty{}^2} = \mathrm{Re}\frac{\Delta\tilde{v}^2}{v_\infty{}^2} \approx \tau^y\left[\psi(0) - \frac{1}{2}\psi''(0)(\omega\tau)^2\right], \tag{17}$$

$$\frac{\alpha'\lambda}{\pi} = \mathrm{Im}\frac{\Delta\tilde{v}^2}{v_\infty{}^2} \approx \tau^y\psi'(0)\,\omega\tau. \tag{18}$$

Near the critical region ($x \gg 1$), we have

$$\psi(x) = A_\infty x^{-y}, \tag{19}$$

where A_∞ is a real quantity,

$$(v_\infty{}^2 - v^2)/v_\infty{}^2 = A_\infty\omega^{-y}\cos(\pi y/2), \tag{20}$$

$$\alpha'\lambda/\pi = A_\infty\omega^{-y}\sin(\pi y/2). \tag{21}$$

The relationships (17), (18), and (20), (21) allow us to formulate the following conclusions which apply to the nematic and isotropic phases and which can be checked experimentally.

1. The asymptotic behavior of the absorption and dispersion in the limiting cases of low and high frequencies is governed by the same critical exponent y:

$$\frac{v_\infty{}^2 - v^2}{v_\infty{}^2} \sim \frac{\alpha'\lambda}{\omega\tau} \sim A(T) \sim \tau^y, \quad \omega\tau \ll 1;$$
$$\frac{v_\infty{}^2 - v^2}{v_\infty{}^2} \sim \alpha'\lambda \sim \omega^{-y} \tag{22}$$

$$\frac{v_\infty{}^2 - v^2}{v_\infty{}^2 A(T)} = \varphi_1(\omega\tau) \sim \frac{\alpha'\lambda}{A(T)} = \varphi_2(\omega\tau) \sim (\omega\tau)^{-y}, \quad \omega\tau \gg 1. \tag{23}$$

2. In the limit $\omega\tau \to \infty$ the ratio of the dispersion to the absorption tends to a constant value:

$$\frac{\mathrm{Re}\,\psi(x)}{\mathrm{Im}\,\psi(x)} = \frac{v_\infty{}^2 - v^2}{v_\infty{}^2\alpha'\lambda} = \frac{\varphi_1(\omega\tau)}{\varphi_2(\omega\tau)} = \mathrm{ctg}\frac{\pi}{2}y. \tag{24}$$

It is clear from Figs. 3, 4, 5, and 7 that both conclusions deduced from dynamic scaling are borne out by the experimental results. The values of the critical exponent y are the same for the dispersion and absorption in both substances, but they differ slightly between the nematic and isotropic phases (Table I). The value of the ratio $\mathrm{Re}\psi/\mathrm{Im}\psi = \varphi_1/\varphi_2 = 1 \pm 0.2$ applies to both substances in the isotropic and nematic phases, which is in agreement with the critical exponent $y \approx 0.5$.

It is worth noting the value of the exponent $y = \alpha/z \approx 0.5$, which is obtained for the nematic phase. We are not convinced that the lower value $y \approx 0.4$ for the isotropic phase is asymptotic and does not increase to 0.5 in the limit $\omega\tau \to \infty$. The value $y = 0.5$ corresponds to the self-consistent field approximation, but it is important to note that the critical exponents of the specific heat ($\alpha < 0.5$ - Ref. 2) and of the relaxation time ($z < 1$, see the next section) do not agree with the corresponding exponents obtained in the self-consistent field approximation ($\alpha = 0.5, z = 1$).

Clearly, these values, which require introduction of a fitting parameter T^* in the definition, cannot be regarded as the real (asymptotic) critical exponents and only selection of the relaxation time as the scaling factor gives the true power-law behavior.

The scaling description of the acoustic relaxation process is attractive if only because it makes it possible to avoid the use of a large number of fitting parameters in the expan-

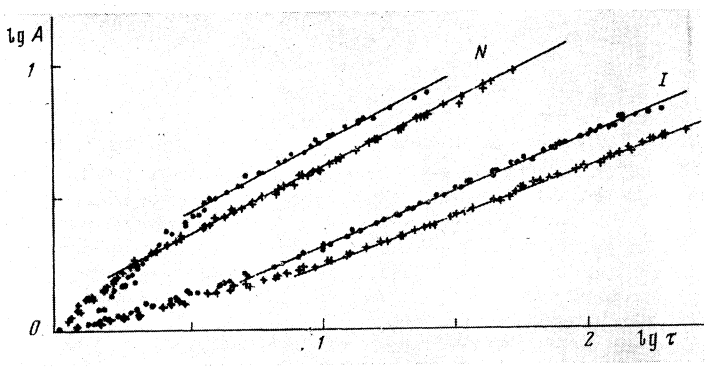

FIG. 7. Asymptotic behavior of the absorption of sound in both phases of MBBA (●) and BMOAB (+) in the $\omega\tau \ll 1$ case; $A \propto \alpha'\lambda/\omega\tau$ (see Eq. (22)].

sion (11), the validity of which is doubtful. It is worth noting only that the critical exponent y is close to the average-field value 0.5.

4. DISCUSSION OF EXPERIMENTAL RESULTS. EXPLICIT FORM OF FUNCTIONS DESCRIBING ACOUSTIC RELAXATION

A. Relaxation time

We shall compare the relaxation time, found by us by deriving homogeneous functions, with the results of direct measurements. In the case of the isotropic phase of MBBA there are data on $\tau(T)$ obtained from measurements of the line width of the anisotropic Rayleigh scattering of light[9] and from induced birefringence.[18] The results are qualitatively close to one another and give the value $\tau \sim 1 \mu$sec for $T \approx T_{NI}$. It is clear from Fig. 8 that the temperature dependences of our results are in agreement with those reported in Ref. 18, which are clearly the most accurate. Therefore, the results from Ref. 18 will be used to link our values of τ to the absolute time scale.

We shall represent the relaxation time by

$$\tau = \chi \nu, \tag{25}$$

where χ is the susceptibility and v is some kinetic coefficient. If we assume that the coefficient v is independent of the proximity to the transition point and that its temperature dependence (like that of the shear viscosity) is

$$\nu = \nu_0 e^{\Theta/T}, \tag{26}$$

we find that the relaxation time calculated from Eq. (25) agrees with the experimental data. We then obtain $\Theta = 4200$ K. The temperature dependence of the susceptibility of MBBA was taken from Ref. 19. It was found that MBBA, like BMOAB (Ref. 4), did not satisfy the Curie law $\chi \propto t^{-1}$: the susceptibility and, consequently, the relaxation time had a characteristic "beak" in the isotropic phase close to T_{NI} ($z < 1$). In Ref. 4 the deviations from linearity were described by fluctuation corrections going beyond the Ornstein-Zernike approximation. The difference between the values of the relaxation times of MBBA and BMOAB (approximately a factor of 2) was clearly due to the corresponding difference in the shear viscosity.

Since independent data on the relaxation time in the nematic phase were not available, the linkage to the absolute time scale was made by matching the experimental dependence $\varphi_2(\omega\tau)$ to that found by calculation (see Fig. 6). The relaxation time in the nematic phase of both substances was several times greater than the relaxation time in the isotropic phase. The reasons for this difference were not clear.

B. Amplitude of the critical absorption and dispersion

We shall compare the amplitudes of the critical absorption and dispersion [see Eqs. (2) and (3)] with the anomalous parts of the specific heat (ΔC_P) taken from Ref. 2. It is clear from Fig. 9 that, within the limits of the experimental error, the temperature dependences of $A(T)$ and $\Delta C_P/(C_P)_0$ are identical [$(C_P)_0$ is the regular part of the specific heat]. Moreover, the coefficient of proportionality g is close to unity. The values of the coefficient $g = A(C_P)_0/\Delta C_P$ are listed below:

	MBBA	BMOAB
isotropic phase:	0.85 ± 0.08	1.06 ± 0.05
nematic phase:	0.70 ± 0.17	0.75 ± 0.10

The product $A(T)(C_P)_0/\Delta C_P$ for the isotropic phase was calculated by Imuro and Okano,[7] who followed Fixman[20] and postulated identical values of the anomalous parts of the specific heats C_P and C_V. As shown in Ref. 21, this corresponds to neglect of the pressure dependence of the

TABLE I. Values of critical exponent y

	Isotropic phase		Nematic phase	
	MBBA	BMOAB	MBBA	BMOAB
$\omega\tau \ll 1$ (absorption)	0,36±0,05	0,40±0,05	0,50±0,05	0,50±0,05
$\omega\tau \gg 1$ (dispersion)	0,45±0,10	0,48±0,10	0,43±0,05	0,50±0,05
$\omega\tau \gg 1$ (absorption)	≈0,4	≈0,4	0,50±0,05	0,50±0,05

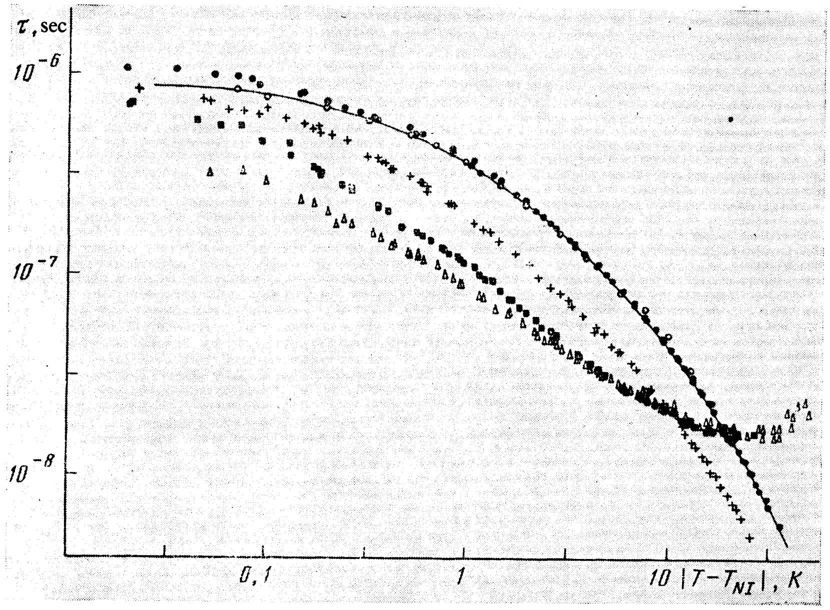

FIG. 8. Relaxation times of MBBA and BMOAB near the *NI* transition: ●), ■) MBBA; +), △) BMOAB; ●) +) *I* phase; ■), △) *N* phase; ○) results taken from Ref. 18; the continuous curve represents τ calculated using Eqs. (25) and (26).

transition temperature. If $dT_{NI}/dP = 0$, then

$$g=A(T)(C_P)_0/\Delta C_P=(C_P)_0/(C_V)_0-1=\gamma_0-1. \tag{27}$$

An allowance for the dependence of T_{NI} on P gives, in the first approximation,[21]

$$g=(\gamma_0-1)+2\gamma_0(\partial P/\partial T)_V(dT_{NI}/dP). \tag{28}$$

Using the experimental values of the parameters occurring in Eq. (28), which are $(\partial P/\partial T)_V \approx 1$ MPa/K, $\gamma_0 \approx 1.2$ (Ref. 22), and $dT_{NI}/dP = 0.35$ k/MPa (Ref. 8), we obtain an estimate $g \approx 1$ (with an error of the order of 10-20%), which is in good agreement with the experimental results.

C. Explicit form of universal functions

The explicit forms of the functions $\varphi_1(\omega\tau)$ and $\varphi_2(\omega\tau)$ for the isotropic phase are close to those given in Ref. 7 (Fig. 4), which are based on the Ornstein-Zernike approximation [see Eq. (8)]:

$$\varphi_1(\omega\tau)=\operatorname{Re}F_2(x)=\left(\frac{4}{\omega\tau}\right)^{1/2}\left[\frac{2}{\omega\tau}+\left(1+\frac{4}{\omega^2\tau^2}\right)^{1/2}\right]^{-1/2},$$

$$\varphi_2(\omega\tau)=\operatorname{Im}F_2(x)=$$

$$\left(\frac{4}{\omega\tau}\right)^{1/2}\left\{\left[\frac{2}{\omega\tau}+\left(1+\frac{4}{\omega^2\tau^2}\right)^{1/2}\right]^{1/2}-\left(\frac{4}{\omega\tau}\right)^{1/2}\right\}. \tag{29}$$

It should be noted that even near the usual critical point, where the self-consistent field approximation does not apply, the correlation function differs little from the Ornstein-Zernike correlation function.[14] The form of the universal functions $\varphi_1(\omega\tau)$ and $\varphi_2(\omega\tau)$ for the nematic phase can be approximated by the expressions

$$\begin{aligned}\varphi_1(\omega\tau)&=m\operatorname{Re}F_1(x)+(1-m)\operatorname{Re}F_2(x),\\ \varphi_2(\omega\tau)&=m\operatorname{Im}F_1(x)+(1-m)\operatorname{Im}F_2(x).\end{aligned} \tag{30}$$

The best agreement is obtained for $m = 0.75$. This value is close to the results of calculations carried out in the self-consistent field approximation (see Sec. 3 and Fig. 6), but in contrast to the latter it is independent of proximity to the transition point. This corresponds to the same temperature dependences of A_1 and A_2 in Eq. (6), providing an additional argument in support of the scaling description.

6. CONCLUSIONS

The universality of the critical dynamics of nematic liquid crystals and the nature of the asymptotes of the universal functions make it possible to put forward new ideas on the nature of the *NI* transition. Clearly, the tensor nature of the

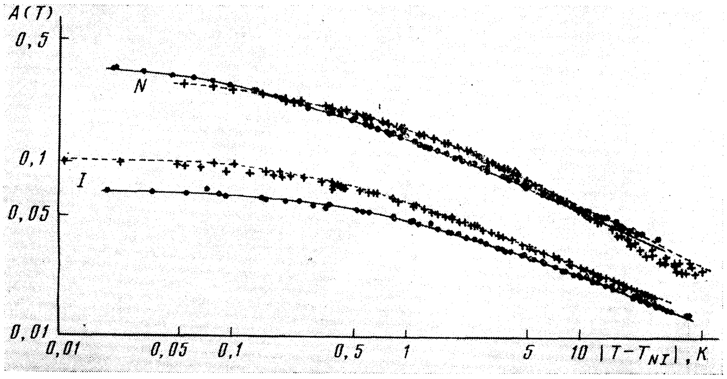

FIG. 9. Relationship between the amplitude of the critical absorption and the anomalous part of the specific heat: the continuous curves represent the specific heat of MBBA and BMOAB; $A(T)$: ●) MBBA; +) BMOAB.

order parameter and the associated first-order character of the *NI* transition are the main reasons for the difficulties encountered when an attempt is made to describe this transition in the self-consistent field approximation in spite of the relatively small value of the Ginzburg number ($\mathrm{Gi} \sim 10^{-3}$) obtained ignoring the cubic invariant in the Landau expansion. The existence of this cubic invariant causes breakdown of the universal relationships between the temperature dependences of the anomalies of the physical quantities. The use of the relaxation time as the scaling factor restores the universality. This universality can also be restored if in place of $T - T^*$ we select the susceptibility or the specific heat as the scaling factor. This selection of the scaling factor is more natural in the description of equilibrium properties. Although the reconstructed universal picture is characterized clearly by the average-field critical exponents, the approach used is characteristic of the scaling procedure.

In particular, there is no need to separate the fluctuation contribution to the anomalies of physical properties from the contribution associated with the temperature dependence of the order parameter and in this sense an allowance for fluctuations cannot be reduced simply to small corrections.

1) Both substances were prepared from materials supplied by the Scientific-Research Institute of Organic Intermediate Products and Dyes, Moscow without any additional purification.

2) The quantity v_∞ may, in principle, differ from the velocity of sound at very high frequencies, since critical relaxation mechanisms are active when $\omega\tau \gg 1$.

3) As a result of this procedure, which does not imply the use of a specific theoretical model, the relaxation time is determined accurately apart from a factor which is the same for all the experimental points.

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[1] W. H. De Jeu, Rev. Mod. Phys. (in press).

[2] M. A. Anisimov, V. M. Mamnitskiĭ, and E. L. Sorkin, paper presented at Ninth Intern. Liquid Crystal Conf., Bangalore, India, 1982. M. A. Anisimov, V. M. Mamnitskiĭ, and E. L. Sorkin, Inzh. Fiz. Zh. **39**, 1110 (1980).

[3] H. Kneppe, V. Reiffenrath, and F. Schneider, Chem. Phys. Lett. **87**, 59 (1982).

[4] L. V. Adzhemyan, L. Yu. Adzhemyan, A. Ts. Val'kov, L. A. Zubkov, I. V. Mel'nik, and V. P. Romanov, Zh. Eksp. Teor. Fiz. **87**, 1244 (1984) [Sov. Phys. JETP **60**, 712 (1984)].

[5] P. G. de Gennes, Superconductivity of Metals and Alloys, Benjamin, New York, 1966 (Russ. Transl., Mir, M., 1977).

[6] M. A. Anisimov, Usp. Fiz. Nauk **114**, 249 (1974) [Sov. Phys. Usp. **17**, 722 (1975)].

[7] H. Imura and K. Okano, Chem. Phys. Lett. **19**, 387 (1973).

[8] E. Kuss, Mol. Cryst. Liq. Cryst. **47**, 71 (1978); H. Kneppe and F. Schneider, Mol. Cryst. Liq. Cryst. **65**, 23 (1981).

[9] T. W. Stinson and J. D. Litster III, Phys. Rev. Lett. **25**, 503 (1970).

[10] D. Eden, C. W. Garland, and R. C. Williamson, J. Chem. Phys. **58**, 1861 (1973).

[11] S. Nagai, P. Martinoty, and S. Candau, J. Phys. (Paris) **37**, 769 (1976).

[12] V. P. Voronov and V. M. Merkulov, Sb. Nauchn. Tr. Vses. Nauchno-Issled. Inst. Fiz.-Tekh. Radiotekh. Izmer. 64 (1981).

[13] R. A. Ferrell and J. K. Bhattacharjee, Phys. Rev. B **23**, 2434 (1981).

[14] A. Z. Patashinskiĭ and V. L. Pokrovskiĭ, Fluktuatsionaya teoriya fazovykh perekhodov, Nauka, M., 1975 (Fluctuation Theory of Phase Transitions, Pergamon Press, Oxford, 1979).

[15] L. D. Landau and I. M. Khalatnikov, Dokl. Akad. Nauk SSSR **96**, 469 (1954).

[16] H. Gasparoux, J. R. Lalanne, and B. Martin, Mol. Cryst. Liq. Cryst. **51**, 221 (1979).

[17] R. A. Ferrell and J. K. Bhattacharjee, Phys. Lett. A **86**, 109 (1981).

[18] G. K. L. Wong and Y. R. Shen, Phys. Rev. A**10**, 1277 (1974).

[19] E. Gulari and B. Chu, J. Chem. Phys. **62**, 798 (1975).

[20] M. Fixman, J. Chem. Phys. **36**, 1957 (1962).

[21] M. A. Anisimov, Issledovanie ravnovesnykh i kineticheskikh svoĭstv vblizi kriticheskikh tochek zhidkosteĭ (Investigation of Equilibrium and Kinetic Properties Near Critical Points of Liquids, Doctoral Thesis), M., 1974.

[22] A. P. Kapustin, Élektroopticheskie i akusticheskie svoĭstva zhidkikh kristallov (Electrooptic and Acoustic Properties of Liquid Crystals), Nauka, M., 1973.

Translated by A. Tybulewicz