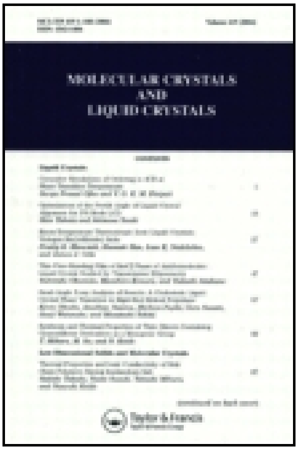

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E. M. Averyanov [a]

[a] L. V. Kirensky Institute of Physics, Krasnoyarsk, 660036, USSR

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# Longitudinal Susceptibility of a Uniaxial Nematic†

E. M. AVERYANOV

*L. V. Kirensky Institute of Physics, Krasnoyarsk, 660036, USSR*

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The relation between the longitudinal susceptibility $\chi$ and the order parameter temperature dependence measured experimentally has been established for uniaxial nematics within the framework of the Landau–de Gennes theory. The absolute values of $\chi$ for the nematic phase, with MBBA as an example, have been obtained from experimental data for the first time and the critical behaviour of $\chi$ has been studied.

*Keywords: nematics, susceptibility*

## I. INTRODUCTION

The order parameter of a uniaxial nematic is the symmetric tensor[1]

$$S_{\alpha\beta} = S(n_\alpha n_\beta - \delta_{\alpha\beta}/3), \tag{1}$$

where $n_{\alpha,\beta}$ are the director $\vec{n}$ components, $S = \langle 3\cos^2\theta - 1\rangle/2$, $\theta$ is the angle made by the long molecular axis with $\vec{n}$ and the brackets $\langle\ldots\rangle$ denote the ensemble average. The nematic response on the field $h$ conjugated thermodynamically to the modulus $S$ is characterized by the longitudinal susceptibility[2]

$$\varkappa = \left(\frac{\partial S}{\partial h}\right)_{T;h\to 0} \tag{2}$$

The data on the value of $\chi$ and its temperature dependence in the nematic phase are necessary to select liquid-crystalline compounds with the maximum response as well as to answer a number of important physical questions.[1]

However any experimental data on $\chi$ in the nematic phase are absent up to now. The direct determination of $\chi$ in a nematic from the measurement of the birefringence $\Delta n \sim S$ in a magnetic or electric field is impossible, since the change $\delta(\Delta n)$ in the field $H \| \vec{n}$ due to the suppression of transverse thermal fluctuations of the local director $\vec{n}$ $(\vec{r})$ depends linearly on $H$ (or $|E|$)[1] while to determine $\chi$ the

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change $\delta(\Delta n) \sim H^2$ is necessary. In sufficiently weak fields the linear effect is two order stronger than the quadratic one.[3]

The other approach to determine $\chi$ is based on the Landau-de Gennes theory, when the thermodynamical potential density $\Delta\Phi$ of a nematic is supposed to be the power function of the invariants $Sp\hat{S}^2 \sim S^2$ and $Sp\hat{S}^3 \sim S^3$ and can be presented by the following series

$$\Delta\Phi = \frac{1}{2}\alpha_2 S^2 + \sum_{n>2}^{N} \frac{1}{n}\alpha_n S^n. \tag{3}$$

Here $\alpha_2 = \alpha(T - T^*)$, where $T^*$ is the absolute stability limit of the isotropic phase and the rest coefficients $\alpha_n$ are assumed to be temperature independent within the sufficiently narrow range of the nematic phase. The peculiarity of real nematics is that the mutually consistent description of the values of various physical parameters and their temperature behaviour is possible only when many terms in Equation (3) are taken into account.[4,5] Moreover the parameters $\alpha_3 < 0$, $\alpha_4 < 0$ $\alpha_5 > 0$ and $\alpha_6 > 0$ are strongly correlated between themselves and all the expansion terms beginning from $\alpha_4 S^4$ turn to be of the same order in the vicinity of the nematic-isotropic liquid (N-I) transition. Taking into account the additional expansion terms makes this description pure empirical.

On the other hand, to describe the same set of experimental data the signs and values of the expansion coefficients in Equation (3) have to depend essentially on the number of the terms taken into account.[4,6] In this case the result of the expression of $\chi$ by the expansion coefficients with using the relation[2]

$$\chi = (\partial^2\Phi/\partial S^2)^{-1}_{S_e} \tag{4}$$

becomes uncertain. Here the equilibrium value $S_e$ is the solution of the equation $\partial\Phi/\partial S = 0$, which surely includes a finite number of the terms in Equation (3).

In this paper a new approach is proposed to determine the nematic longitudinal susceptibility $\chi$ allowing to express it by the temperature dependence of the modulus $S$. The theoretical part of the approach is presented in the second section. The third section includes the analysis of the critical behaviour of $\chi$ in the nematic phase of MBBA and the comparison with the results of independent measurements of the other parameters having singularities near the N-I transition temperature $T_c$.

## II. NEMATIC LONGITUDINAL SUSCEPTIBILITY AND TEMPERATURE DEPENDENCE OF THE ORDER PARAMETER

To go further it is important to considerate the character of the temperature dependence $\alpha_2(T)$ in Equation (3). This coefficient is the inverse susceptibility $\chi_i^{-1}$ of the isotropic phase and its temperature dependence can be cleared up from the experiments on the critical behaviour of various physical parameters.[1,4] All known data show that for nematics having not the low temperature smectic phases the dependence $\alpha_2 \sim (T - T^*)$ is valid within the wide temperature region $T > T_c$ except for the narrow range about a fraction of degree near $T_c$. So the thermodynamical potential density of a uniaxial nematic in the field $h$ conjugated to the modulus $S$ can be written in the form

$$\Delta\Phi = \frac{1}{2}\alpha(T - T^*)S^2 + \sum \frac{1}{n}\alpha_n S^n - hS, \tag{5}$$

where $\alpha_n \neq \alpha_n(T)$. The equation of state

$$\alpha(T - T^*)S + \sum \alpha_n S^{n-1} - h = 0 \tag{6}$$

is the functional relation $f(x, y, z) = 0$ of the variables $x = S$, $y = h$ and $z = T$. So with using the next known identities[7]

$$\left(\frac{\partial x}{\partial y}\right)_z \cdot \left(\frac{\partial y}{\partial z}\right)_x \cdot \left(\frac{\partial z}{\partial x}\right)_y = -1, \quad \left(\frac{\partial z}{\partial x}\right)_y = \left[\left(\frac{\partial x}{\partial z}\right)_y\right]^{-1} \tag{7}$$

the relation can be obtained from Equation (6)

$$\left(\frac{\partial S}{\partial h}\right)_T = -\frac{1}{\alpha S}\left(\frac{\partial S}{\partial T}\right)_h, \tag{8}$$

the form of which depends neither on the expansion terms number $N$ in Equations (3) and (6) nor on the concrete values $n$ taken into account. In the limit $h \to 0$ the value of $S$ in Equation (8) transfers to the equilibrium value $S_e$ being the solution to Equation (6) at $h = 0$ and describing the experimental dependence $S(T)$ when the sufficient number of the expansion terms in Equation (3) is taken into account. Indeed for a set of real nematics[5,8,9] the experimental dependence $S(T)$ can be described using Equation (3) within the whole nematic range with the corresponding number of the terms being taken into account for each compound.

Finally using the variable $t = 1 - T/T_0$, where $T_0$ is the temperature of the absolute stability limit of the nematic phase the expression of $\chi$ by the magnitudes measured experimentally can be obtained

$$\chi = \frac{1}{\alpha T_0} \cdot \frac{\partial(\ln S)}{\partial t}. \tag{9}$$

The parameter $\alpha$ can be found from the enthalpy discontinuity $\Delta H = \alpha S_c^2 T_c/2$, where $S_c = S(T_c)$. Equation (9) is applicable to a wide set of systems, whose thermodynamical potential in the field $h$ has the form of Equation (5). For the particular cases of the theory taking into account a finite number of the terms with $n > 2$ in Equation (3) the substitution of the dependences $S_e(t)$ obtained from the equation $\partial\Phi/\partial S = 0$ to Equation (9) results in the same expressions for $\chi(t)$ as the ones obtained from Equation (4).[1,2,4,10]

## III. LONGITUDINAL SUSCEPTIBILITY OF THE NEMATIC PHASE OF MBBA

The value of $\chi$ obtained using the experimental data on $S$ in Equation (9) includes the contribution from the transverse thermal fluctuations of the local director $\vec{n}$ $(\vec{r})$ due to the principle of conservation of the modulus for a nematic as a degenerate system.[11,12] However the negligible relative change $\delta(\Delta n)/\Delta n$ in strong fields due to the suppression of the director fluctuations[1,3] and Equation (9) show that the main contribution to the value of $\chi$ is made by the temperature dependence of local orientational molecular ordering.

To obtain $\chi$ using Equation (9) it is important to choose the physical magnitude for the determination of the modulus $S$. Rotational braking of molecules around their long axes and the biaxiality of the molecular second-rank tensor $\hat{\gamma}$ result in the macroscopic anisotropy

$$\Delta M \sim (S\Delta\gamma + G\Delta\gamma'/2) \tag{10}$$

of the corresponding magnitude to be determined not only by the component $S = S_{zz}$ but also by the biaxiality $G = S_{xx} - S_{yy}$ of the microscopic tensor of orientational molecular ordering

$$S_{ii} = \langle 3\cos^2\theta_{in} - 1\rangle/2, \qquad (i = x, y, z) \tag{11}$$

where $\theta_{in}$ is the angle made by the $i$-th axis of the molecular frame with the director $\vec{n}$. The designations used in Equation (10) are following

$$\Delta\gamma = \gamma_{zz} - (\gamma_{xx} + \gamma_{yy})/2, \qquad \Delta\gamma' = \gamma_{xx} - \gamma_{yy}. \tag{12}$$

With using the dielectric constant anisotropy $\Delta\varepsilon$ at optical frequencies as $\Delta M$ in Equation (10) the biaxiality of the tensor $\hat{S}$ and the molecular polarizability $\hat{\gamma}$ is significantly less manifested than with using the diamagnetic susceptibility anisotropy.[13] Taking into account the local field anisotropy of a light wave results in the right part in Equation (10) to be multiplied by the value $(1 + \sigma_0 + \sigma_1)^{-1}$, where $\sigma_0$ does not depend on the temperature and $\sigma_1 \sim S$ with the relations $\sigma_0 \simeq 0.2$ and $\sigma_1/\sigma_0 \simeq 0.1$ being valid even for nematics with large local field anisotropy.[14] Moreover the sum $(\sigma_0 + \sigma_1)$ can be vanished choosing the nematic refractive indices within the corresponding spectral region, the ratio $\Delta\gamma'/\Delta\gamma$ being lowered simultaneously.[14] The temperature dependence of the nematic density can be taken into account using

$$\Delta\varepsilon/(\bar{\varepsilon} - 1) = \text{const} \cdot S \tag{13}$$

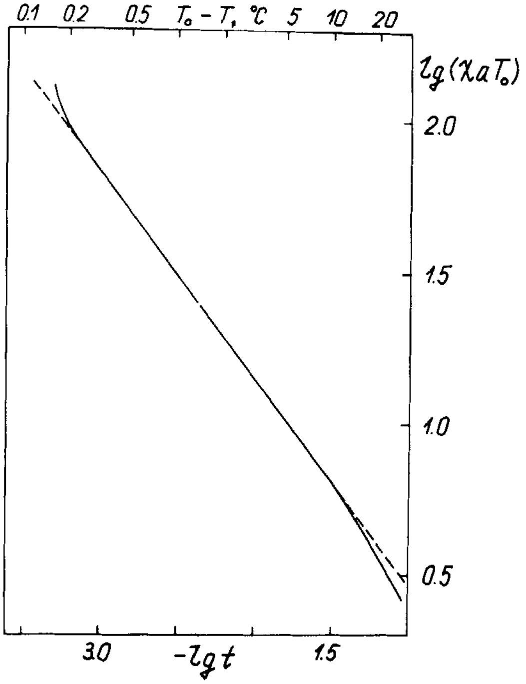
instead of $\Delta\varepsilon = n_{\parallel}^2 - n_{\perp}^2$, where $\bar{\varepsilon} = (n_{\parallel}^2 + 2n_{\perp}^2)/3$, $n_{\parallel,\perp}$ are the refractive indices of a nematic.

In the present work MBBA was chosen for the investigation as an object with the known values of the refractive indices $n_{\|,\perp}$ ($\lambda = 589$ nm) well approximated by the expressions[15]

$$\begin{aligned} n_\perp &= 1.5765 - 0.174\,\tau^{1/2} + 0.253\,\tau, \\ n_\| &= 1.6935 + 0.282\,\tau^{1/2} + 0.243\,\tau, \end{aligned} \tag{14}$$

within the temperature region $0.06° \leq T_c - T \leq 30°$, where $\tau = 1 - T/T_c$ and $T_c = 318.46$ K.[15,16] The local field anisotropy in MBBA is small[17] and doesn't change the dependence $S(T)$ in Equation (13). It is known from the precision measurements of the MBBA heat capacity[18,19] that $T_0$ is 0.1° above the lower boundary $T_c^{(-)}$ of the real two-phase region taken as $T_c$ in refractometric experiments.

The temperature dependence of the product $\chi\alpha T_0$ calculated from Equations (9), (13) and (14) with using $T_0 = T_c + 0.1°$ is shown in Figure. The change of $\chi$ is described by the dependence $\chi \sim t^{-\gamma'}$ with the constant $\gamma' = 0.68$ within the whole experimental temperature region $0.1° \leq T_c - T \leq 20°$. On the other hand according to the acoustic measurements in MBBA[4,20] the ratio $y = \alpha/z = 1/2$ is constant within the same temperature region, where $\alpha$ and $z$ are the effective exponents for the heat capacity and for the relaxation time $\tau$ of the modulus $S$ fluctuations respectively. Using the effective values $\alpha = 0.32–0.35$[18,19] being constant within given temperature region we obtain $z = 0.64–0.70$. It agrees with the



The temperature dependence of the product $\chi\alpha T_0$ (cf. Equation (9)) for the nematic phase of MBBA calculated using Equations (13) and (14).

value of $\gamma'$ mentioned above and shows that for the nematic phase of MBBA the kinetic coefficient $\nu$ in the correlation[2]

$$\tau = \chi \cdot \nu \tag{15}$$

hasn't the own singularity near $T_c$. Thus the results of independent investigations of the dependences $\chi(t)$ and $\tau(t)$ in the nematic phase of MBBA are in good agreement between themselves within the framework of Equation (15).

## IV. CONCLUSION

In conclusion a new possibility should be pointed out to obtain the quantitative information about the susceptibility $\chi$ being the important characteristic of liquid-crystalline compounds. The nematic response $\chi_Q$ on any physical perturbation resulting in the change of the modulus $S$ and being described by the term $-K_Q hS$ in the thermodynamical potential (cf. Equation (5)) is expressed by $\chi$ as $\chi_Q = K_Q \chi$. The resonance influence on the intramolecular degrees of freedom can also play the role of the external perturbation that results in changing the internal molecular state, intermolecular interactions and the modulus $S$ in the sample.

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