Fluctuations of Orientational Order in a Uniaxial Nematic Liquid Crystal with Biaxial Molecules and Its Response to an External Field

E. M. Aver'yanov

Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences,
Akademgorodok, Krasnoyarsk, 660036 Russia
e-mail: aver@iph.krasn.ru
Received June 4, 2002; in final form, October 18, 2002

Abstract—Homogeneous thermal fluctuations of the orientational order parameters S and G of biaxial molecules in a uniaxial nematic liquid crystal are investigated in the framework of the molecular–statistical theory. It is demonstrated that the molecular biaxiality significantly affects the order parameters S and G, their temperature dependences in the nematic phase, the amplitude and the temperature dependence of the order parameter fluctuations in the nematic and isotropic phases, and the character of the transition from the nematic phase to the isotropic liquid phase. It is established that the fluctuations of the parameters S and G in the nematic phase are related to the temperature dependences of S and G and the susceptibilities χ_S and χ_G of the nematic liquid crystal to external fields, which leads to a change in the parameters S and G at a fixed director orientation. Explanations are offered for the known experimental data on the orientational ordering of biaxial molecules under the action of external fields in the isotropic phase of nematic liquid crystals. © 2003 MAIK "Nauka/Interperiodica".

1. INTRODUCTION

The orientational order of lathlike biaxial molecules with respect to the director **n** in a uniaxial calamitic nematic liquid crystal is characterized by the Saupe matrix elements [1]:

$$S_{ij} = \langle 3\cos\theta_{i\mathbf{n}}\cos\theta_{j\mathbf{n}} - \delta_{ij}\rangle/2, \qquad (1)$$

where $\theta_{i\mathbf{n}}$ is the angle between the ith axis of the molecular coordinate system xyz and the director **n** and the brackets $\langle\dots\rangle$ indicate statistical averaging. In the case of molecules with point symmetry group (C_{2v}, D_2, or D_{2h}), when the intrinsic coordinate system of the matrix S_{ij} is chosen as the molecular coordinate system, there are two independent order parameters, namely, $S = S_{zz}$ and $G = S_{xx} - S_{yy}$.

A number of important aspects of the influence of the molecular shape on the transition from a nematic phase to an isotropic liquid phase (N–I transition) were considered in [2–11] within different variants of the molecular–statistical theory and molecular models. However, the specific features of variations in the parameters S and G and the two-phase region in the vicinity of the N–I transition have not been investigated as a function of the molecular biaxiality. Moreover, it has been found that the N–I transition becomes similar in character to a second-order transition with an increase in the degree of molecular biaxiality [2–10]. The elucidation of the origin of this effect requires anal-

ysis of the fluctuations $\overline{\delta S^2}$, $\overline{\delta G^2}$, and $\overline{\delta S\delta G}$ in the range of the N–I transition, which has not been performed to date.

At present, the fluctuations of the macroscopic tensor order parameter $Q_{\alpha\beta}$ in nematic liquid crystals have been studied in detail in the framework of the Landau–de Gennes theory (see [1, 12, 13] and references therein). The molecular–statistical theory of spatially homogeneous and inhomogeneous fluctuations of the order parameter S for uniaxial molecules in the vicinity of the N–I transition was developed in [14–16]. However, the influence of the molecular biaxiality on the amplitude and temperature dependence of the fluctuations $\overline{\delta S^2}$, $\overline{\delta G^2}$, and $\overline{\delta S\delta G}$ in the nematic and isotropic phases remains unclear.

For calamitic and discotic nematic liquid crystals with uniaxial molecules, the relation of the function $S(T)$ to the fluctuations $\overline{\delta S^2}$ and the linear and nonlinear susceptibilities of the nematic phase to external fields, which are thermodynamically conjugate to the magnitude of S, was established in [17, 18]. For nematic liquid crystals with biaxial molecules, the relation of the dependences $S(T)$ and $G(T)$ to the fluctuations $\overline{\delta S^2}$, $\overline{\delta G^2}$, and $\overline{\delta S\delta G}$ is of even greater interest, because the dependence $G(T)$ in the nematic phase exhibits a nonmonotonic behavior [3, 5, 8]. Furthermore, the order parameter G (like the order parameter S

[1]) in the isotropic phase with molecular ordering induced by external fields anomalously increases as the temperature T_{NI} of the N–I transition is approached [19–21]. In this respect, it is important to reveal how the susceptibilities $\chi_S = (\partial S/\partial h)_{T; h \to 0}$ and $\chi_G = (\partial G/\partial h)_{T; h \to 0}$ of the nematic and isotropic phases to the external fields h are related to the dependences $S(T)$ and $G(T)$ and also to the fluctuations $\overline{\delta S^2}$, $\overline{\delta G^2}$, and $\overline{\delta S \delta G}$.

In this work, the above problems were analyzed in terms of the molecular–statistical theory. Expressions were derived for the free energy of nonequilibrium and equilibrium states of the nematic phase, and the influence of the biaxiality on the N–I transition was investigated. Moreover, the fluctuations $\overline{\delta S^2}$, $\overline{\delta G^2}$, and $\overline{\delta S \delta G}$ in the nematic and isotropic phases were examined. Consideration was given to the response of a nematic liquid crystal with biaxial molecules to external fields, which leads to a change in the parameters S and G. The relation of the susceptibilities χ_S and χ_G to the temperature dependences of the parameters S and G and their fluctuations was revealed. An interpretation was offered for the experimental data obtained in [19–21].

2. FREE ENERGIES OF A NEMATIC LIQUID CRYSTAL IN NONEQUILIBRIUM AND EQUILIBRIUM STATES

In a uniaxial calamitic nematic liquid crystal consisting of molecules with the aforementioned symmetry, the orientation of the molecular coordinate system xyz with respect to the director coordinate system XYZ ($\mathbf{n} \parallel Z$) is characterized by the Euler angles $\Omega(\phi, \theta, \psi)$. Here, ϕ and θ are the azimuthal and polar angles of the long molecular axis z in the coordinate system XYZ, respectively; and ψ is the rotation angle of the molecule about the z axis. With the use of the orientational distribution function of molecules $f(\Omega)$, we can write

$$S \equiv \langle P_2 \rangle = \int P_2(\cos\theta) f(\Omega) d\Omega,$$
$$G \equiv \langle D(\theta, \psi) \rangle = \int (1 - P_2) \cos 2\psi f(\Omega) d\Omega, \quad (2)$$

where $P_2(\cos\theta)$ is the Legendre polynomial. The quantity G characterizes the degree of hindrance to the rotation of molecules about their long axes z. For given parameters S and G, reasoning from the principle of the maximum informational entropy [22] with due regard for formulas (2) and the normalizing condition for $f(\Omega)$,

the function $f(\Omega)$ can be represented in the following form [23]:

$$f(\Omega) = \frac{1}{8\pi^2 Z} \exp(\lambda_P P_2 + \lambda_D D),$$
$$Z = \frac{1}{8\pi^2} \int \exp(\lambda_P P_2 + \lambda_D D) d\Omega. \quad (3)$$

The parameters S and G can be defined by the expressions

$$S = \partial \ln Z / \partial \lambda_P, \quad G = \partial \ln Z / \partial \lambda_D, \quad (4)$$

which form a system of equations for determining $\lambda_P(S, G)$ and $\lambda_D(S, G)$.

We will consider the nematic and isotropic phase at a constant volume. The difference between the free energies of the nematic and isotropic phases per molecule can be written in the form

$$\Delta F = E(S, G) + kT \int \ln[8\pi^2 f(\Omega)] f(\Omega) d\Omega, \quad (5)$$

where $E(S, G)$ is the anisotropic part of the internal energy. In the mean-field approximation, with allowance made for the results of analyzing the intermolecular interactions in nematic liquid crystals [5, 8, 23, 24], we can write

$$E(S, G) = -(u/2)(S + \lambda_1 G)^2, \quad (6)$$

where $u > 0$ and the parameter λ_1 is determined by the molecular properties. For anisotropic dispersion intermolecular interactions in the mesophase, this parameter has the form

$$\lambda_1 = (\gamma_{xx} - \gamma_{yy})/(2\gamma_{zz} - \gamma_{xx} - \gamma_{yy}). \quad (7)$$

Here, γ_{ii} are the molecular polarizability tensor components averaged over the entire spectral range. At $0 \le \lambda_1 \le 1$, molecules have polarizability ellipsoids that are either prolate ($\lambda_1 < 1/3$) or oblate ($\lambda_1 > 1/3$) along the z axis and, correspondingly, form either calamitic or discotic nematic phases. Within the approaches developed in [11, 25], the parameter λ_1 for the same form of $E(S, G)$ [expression (6)] can be associated with the sizes of molecules characterized by an ellipsoidal or more complex shape.

Substitution of formulas (3) and (6) into expression (5) gives the functional of the nonequilibrium free energy:

$$\Delta F = -\frac{u}{2}(S + \lambda_1 G)^2$$
$$+ kT[\lambda_P S + \lambda_D G - \ln Z(\lambda_P, \lambda_D)], \quad (8)$$

where λ_P and λ_D are the functions of the parameters S and G. Then, taking into account relationships (4), we have

$$(\partial F/\partial S)_T = -u(S + \lambda_1 G) + kT\lambda_P,$$
$$(\partial F/\partial G)_T = -u\lambda_1(S + \lambda_1 G) + kT\lambda_D. \quad (9)$$

The conditions of the thermodynamic equilibrium $(\partial F/\partial S)_T = (\partial F/\partial G)_T = 0$ allow us to obtain the relationships

$$\lambda_P(S, G) = \frac{u}{kT}(S + \lambda_1 G),$$
$$\lambda_D(S, G) = \frac{u\lambda_1}{kT}(S + \lambda_1 G) \quad (10)$$

for determining the dependences $S(T)$ and $G(T)$ corresponding to extrema of functional (8). Substitution of relationships (10) into expressions (3) gives the equilibrium distribution function

$$f_e(\Omega) = \frac{1}{8\pi^2 Z_e}\exp\left[\frac{u}{kT}(S + \lambda_1 G)(P_2 + \lambda_1 D)\right],$$
$$Z_e = \frac{1}{8\pi^2}\int\exp\left[\frac{u}{kT}(S + \lambda_1 G)(P_2 + \lambda_1 D)\right]d\Omega, \quad (11)$$

at which functional (5) has an extremum. With the use of relationships (10) in functional (8), we find the equilibrium free energy

$$\Delta F_e = (u/2)(S + \lambda_1 G)^2 - kT\ln Z_e \quad (12)$$

at the extreme points of functional (8). Expression (12) cannot be treated (as was done in monographs [1, 26] and also in [2, 14]) as a functional valid at arbitrary (nonequilibrium) values of S and G and cannot be used for calculating the fluctuations $\overline{\delta S^2}$, $\overline{\delta G^2}$, and $\overline{\delta S \delta G}$. This misinterpretation of expression (12) will be demonstrated below using calculations of $\overline{\delta S^2}$ for a nematic liquid crystal with uniaxial molecules as an example. The difference between the Landau series in the expansions of ΔF [formula (8)] and ΔF_e [formula (12)] in powers of the parameters S and G is shown in Appendix 1, in which the obtained data are also compared with those for uniaxial molecules [26, 27].

3. THE INFLUENCE OF MOLECULAR BIAXIALITY ON THE CHARACTER OF THE N–I TRANSITION

The specific features of the N–I transition with a change in λ_1 in the range $0 \le \lambda_1 < 1/3$ can be revealed using numerical calculations. The relationships

$$S = \int P_2(\cos\theta)f_e(\Omega)d\Omega,$$
$$G = \int D(\theta, \psi)f_e(\Omega)d\Omega \quad (13)$$

represent the system of self-consistent equations, which possesses several solutions. Among them, ΔF exhibits a minimum for the dependences $S_e(T)$ and $G_e(T)$, which satisfy the following conditions:

$$(F_{SS})_{T,e} \ge 0, \quad (F_{GG})_{T,e} \ge 0,$$
$$(F_{SS})_{T,e}(F_{GG})_{T,e} - (F_{SG})_{T,e}^2 \ge 0. \quad (14)$$

Here, the subscript e refers to the derivatives $F_{SS} = \partial^2 F/\partial S^2$, … at thermodynamic equilibrium. For subsequent analysis, we introduce the variances

$$\Delta_P = \langle P_2^2\rangle - S^2, \quad \Delta_{PD} = \langle P_2 D\rangle - SG,$$
$$\Delta_D = \langle D^2\rangle - G^2, \quad (15)$$

which characterize the nonuniformity of the orientational distribution of molecules in a sample. The variances can be written in the form

$$\Delta_P = \partial S/\partial\lambda_P, \quad \Delta_{PD} = \partial S/\partial\lambda_G = \partial G/\partial\lambda_P,$$
$$\Delta_D = \partial G/\partial\lambda_D. \quad (16)$$

With the use of these expressions, we obtain the Jacobian

$$J = \partial(S, G)/\partial(\lambda_P, \lambda_D) = \Delta_P\Delta_D - \Delta_{PD}^2, \quad (17)$$

which is positive in the stability region of the calamitic nematic phase. Therefore, with due regard for relationships (16) and (17), we can write the following expressions:

$$\partial\lambda_P/\partial S = \Delta_D/J, \quad \partial\lambda_D/\partial G = \Delta_P/J,$$
$$\partial\lambda_P/\partial G = \partial\lambda_D/\partial S = -\Delta_{PD}/J. \quad (18)$$

The repeated differentiation of relationships (9) and the use of expressions (18) give

$$(F_{SS})_{T,e} = kT(\Delta_D/J - 1/t),$$
$$(F_{GG})_{T,e} = kT(\Delta_P/J - \lambda_1^2/t), \quad (19)$$
$$(F_{SG})_{T,e} = -kT(\Delta_{PD}/J + \lambda_1/t),$$

where $t = kT/u$ and variances (15) are calculated with the distribution function (11) at $S = S_e$ and $G = G_e$. The limiting temperatures of the stability of the isotropic and nematic phases can be obtained from the condition that the left-hand side of the last inequality in relationships (14) becomes zero. These temperatures obey the equation

$$t = \Delta_P + 2\lambda_1\Delta_{PD} + \lambda_1^2\Delta_D \equiv \Delta_A, \quad (20)$$

in which we used the designations

$$\Delta_A = \langle A^2\rangle - \langle A\rangle^2, \quad A = P_2 + \lambda_1 D. \quad (21)$$

In the isotropic phase, we have $\Delta_P = 1/5$, $\Delta_D = 3/5$, and $\Delta_{PD} = 0$ and formula (20) can be rearranged to give the expression

$$t^*(\lambda_1) = (1 + 3\lambda_1^2)/5 \qquad (22)$$

for the limiting temperature of the stability of the isotropic phase. By substituting this expression into relationships (11) and (13) at fixed λ_1, we find the parameters $S^* = S_e(t^*, \lambda_1)$ and $G^* = G_e(t^*, \lambda_1)$. The simultaneous solution of the system of equations (13) and (20) at fixed λ_1 gives the limiting temperature $t_1(\lambda_1)$ of the stability of the nematic phase and the parameters $S_1 = S_e(t_1, \lambda_1)$ and $G_1 = G_e(t_1, \lambda_1)$. The simultaneous solution of the system of equations (13) and the equation $\Delta F_e = 0$ in expression (12) at fixed λ_1 enables us to obtain the temperature $t_{NI}(\lambda_1)$ and the parameters $S_{NI} = S_e(t_{NI}, \lambda_1)$ and $G_{NI} = G_e(t_{NI}, \lambda_1)$. The dependences of the above parameters on λ_1 are plotted in Figs. 1 and 2.

As can be seen from Fig. 1, an increase in λ_1 leads to an increase in the ratio $(S^* - S_{NI})/(S_{NI} - S_1)$ from 1.762 at $\lambda_1 = 0$ to 2 in the range corresponding to linear dependences of S^*, S_{NI}, and S_1 on λ_1. In this range, the ratios between S^*, S_{NI}, and S_1 do not depend on λ_1 and are determined by formulas (A1.6)–(A1.10) given in Appendix 1. The dependences of the parameters S_{NI} and G_{NI} on λ_1 are qualitatively similar to those obtained in [4, 6, 7, 10] within other variants of the molecular–statistical theory and different models of biaxial molecules. A characteristic feature of the influence of λ_1 on the N–I transition is that a decrease in the two-phase region $(t_1 - t^*)$ with an increase in λ_1 is attended by a weak change in the ratio $(t_{NI} - t^*)/(t_1 - t_{NI})$ from 7.65 at $\lambda_1 = 0$ to 8 at $\lambda_1 \approx 1/3$. It should be noted that the inclusion of the anisotropy of the orientational distribution of molecules over the angle ϕ results in the appearance of the low-temperature biaxial nematic phase N_b. An increase in λ_1 leads to a decrease in the temperature range of the calamitic nematic phase, and the I–N_b continuous transition occurs at $\lambda_1 = 1/3$ [1–3, 9].

The dependences of the parameters G^*, G_{NI}, and G_1 on λ_1 exhibit a nonmonotonic behavior. The change in the ratios between G^*, G_{NI}, and G_1 as a function of λ_1 is associated with the nonmonotonic dependence of $G(T)$ in the nematic phase. The differentiation of expressions (13) with respect to temperature and the solution of the obtained system of equations with respect to the derivatives $\partial S/\partial T$ and $\partial G/\partial T$ give the relationships

$$\frac{\partial S}{\partial T} = -\frac{\langle A \rangle (\Delta_P + \lambda_1 \Delta_{PD})}{T(t - \Delta_A)},$$
$$\frac{\partial G}{\partial T} = -\frac{\langle A \rangle (\Delta_{PD} + \lambda_1 \Delta_D)}{T(t - \Delta_A)}. \qquad (23)$$
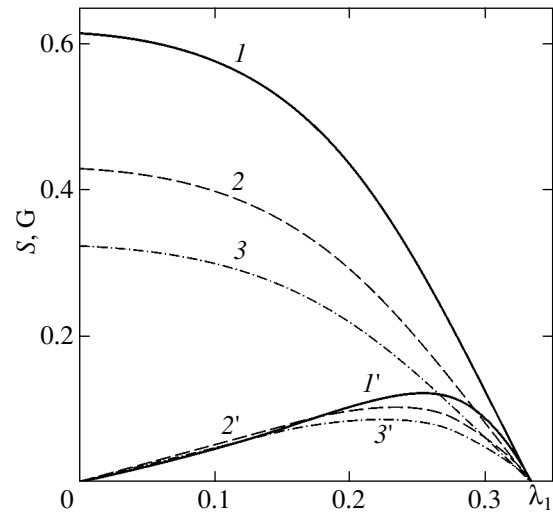

Fig. 1. Dependences of the parameters (*1–3*) S and (*1'–3'*) G on λ_1 at $t = (1, 1')$ t^*, (*2, 2'*) t_{NI}, and (*3, 3'*) t_1.
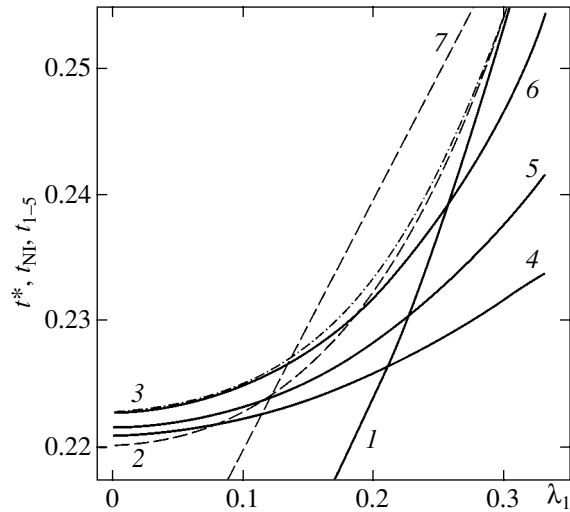
Fig. 2. Dependences of the temperatures (*1*) t^*, (*2*) t_{NI}, (*3*) t_1, (*4*) t_2, (*5*) t_3, (*6*) t_4, and (*7*) t_5 on λ_1. Points (with the abscissas $\lambda_1 = 0.075$, 0.111, 0.122, and 0.184) indicate the intersections of the curve $t_{NI}(\lambda_1)$ with the curves $t_2(\lambda_1)$, $t_3(\lambda_1)$, $t_5(\lambda_1)$, and $t_4(\lambda_1)$, respectively.

A comparison of these relationships with formula (20) shows that the derivatives $\partial S/\partial T$ and $\partial G/\partial T$ diverge at $t = t_1$. The derivative $\partial G/\partial T$ is equal to zero when the following condition is satisfied:

$$\Delta_{PD} = -\lambda_1 \Delta_D. \qquad (24)$$

Since the inequality $\Delta_D \geq 0$ is valid irrespective of the sign of λ_1, the sign of Δ_{PD} is opposite to the sign of λ_1. The solution of the system of equations (13) and (24) at fixed λ_1 gives the quantities $t_2(\lambda_1)$, $S_2 = S_e(t_2, \lambda_1)$, and $G_2 = G_e(t_2, \lambda_1)$ corresponding to the maximum in the
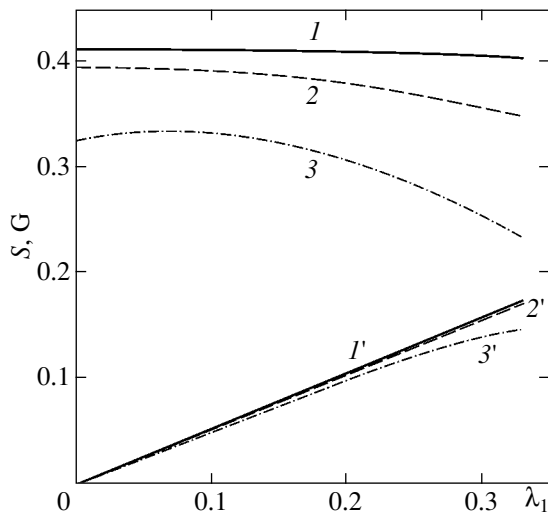
Fig. 3. Dependences of the parameters (*1–3*) S and (*1'–3'*) G on λ_1 at $t = (1, 1')$ t_2, $(2, 2')$ t_3, and $(3, 3')$ t_4.
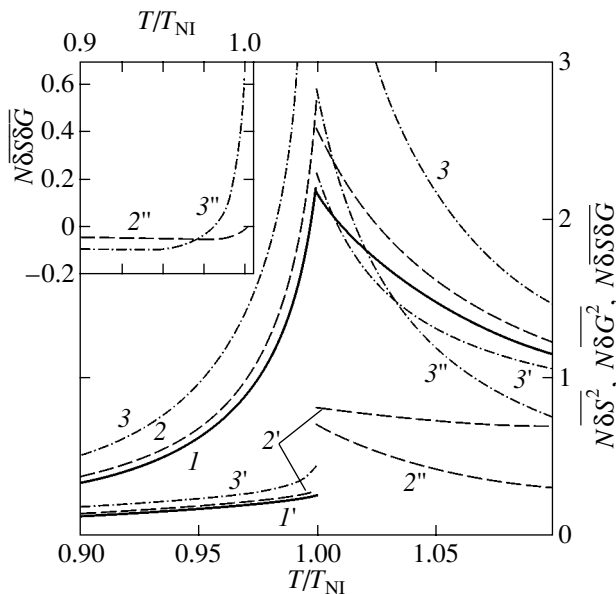

Fig. 4. Dependences of the fluctuations (*1–3*) $\overline{N\delta S^2}$, (*1'–3'*) $\overline{N\delta G^2}$, and (*2", 3"*) $\overline{N\delta S\delta G}$ on T/T_{NI} at $\lambda_1 = (1, 1')$ 0, $(2, 2")$ 0.1, and $(3, 3")$ 0.2.

dependence $G(t)$ at given λ_1. The dependences of these quantities are displayed in Figs. 2 and 3.

It can be seen from Fig. 2 that, at $\lambda_1 \leq 0.075$, the inequality $t_{NI}(\lambda_1) \leq t_2(\lambda_1)$ is satisfied and the function $G(t)$ monotonically increases with an increase in t over the entire range $t \leq t_{NI}$. For molecules with $\lambda_1 > 0.075$, we have $t_{NI}(\lambda_1) > t_2(\lambda_1)$ and an increase in t leads to a nonmonotonic variation in the function $G(t)$. This function increases in the range $t \leq t_2$ from zero at $t = 0$ to the

maximum value G_2 at $t = t_2$ and then decreases in the range $t_2 < t \leq t_{NI}$. The inequality $t^* < t_2$ is valid at $\lambda_1 < 0.212$, and the inequality $t_2 < t^*$ holds at $0.212 < \lambda_1 < 1/3$. The value of S_2 depends weakly on λ_1 and varies from 0.413 to 0.402, which agrees with the experimental data for pure nematic liquid crystals in the absence of low-temperature smectic phases. The dependence $G_2(\lambda_1)$ is nearly linear over the entire range of λ_1 and can be used for estimating the value of λ_1 from the maximum of the experimental dependence $G(t)$ for real liquid crystals.

4. FLUCTUATIONS OF THE ORDER PARAMETERS S AND G

In a nematic liquid-crystal sample containing N molecules, the homogeneous thermal fluctuations $\delta S = S - S_e$ and $\delta G = G - G_e$ lead to the change in the total free energy of the sample $\delta F = N(\Delta F - \Delta F_e)$, which can be written, correct to terms quadratic in δS and δG, in the form

$$
\begin{aligned}
\delta F \\
= \frac{N}{2}[(F_{SS})_{T,e}\delta S^2 + 2(F_{SG})_{T,e}\delta S\delta G + (F_{GG})_{T,e}\delta G^2].
\end{aligned}
\tag{25}
$$

The distribution function $w \sim \exp(-\delta F/kT)$ for the quantities $x_1 = (N)^{1/2}\delta S$ and $x_2 = (N)^{1/2}\delta G$ has the following form:

$$
w(x_1, x_2) = \frac{\sqrt{\beta}}{2\pi}\exp\left(-\frac{1}{2}\beta_{ik}x_ix_k\right),
\tag{26}
$$

$$
i, k = 1, 2,
$$

where the matrix elements β_{ik} and the matrix determinant β are defined by the relationships

$$
\beta_{11} = \Delta_D/J - 1/t, \quad \beta_{12} = \beta_{21} = -(\Delta_{PD}/J + \lambda_1/t),
$$

$$
\beta_{22} = \Delta_P/J - \lambda_1^2/t, \quad \beta = (t - \Delta_A)/Jt.
\tag{27}
$$

According to [28], averaging with the use of function (26) gives

$$
\overline{x_ix_k} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} x_ix_k w(x_1, x_2)dx_1dx_2 = \beta_{ik}^{-1},
\tag{28}
$$

where β_{ik}^{-1} is the element of the matrix that is inverse to the matrix β_{ik}. As a result, we obtain

$$
\overline{N\delta S^2} = \frac{t\Delta_P - \lambda_1^2 J}{t - \Delta_A}, \quad \overline{N\delta G^2} = \frac{t\Delta_D - J}{t - \Delta_A},
$$

$$
\overline{N\delta S\delta G} = \frac{t\Delta_{PD} + \lambda_1 J}{t - \Delta_A}.
\tag{29}
$$

The temperature dependences of these fluctuations are depicted in Fig. 4. Let us consider the cases of uniaxial and biaxial molecules.

4.1. Uniaxial Molecules

At $\lambda_1 = \Delta_{PD} = 0$, the fluctuations δS and δG are statistically independent and $\overline{\delta S \delta G} = 0$. For both phases, we have $N \overline{\delta G^2} = \Delta_D$. In the nematic phase, the following relationships are valid:

$$\Delta_D = 3/5 - 6S/7 + 9\langle P_4\rangle/35,$$
$$\langle P_4\rangle = (7 + 5S - 35t)/12, \tag{30}$$

where $P_4(\cos\theta)$ is the Legendre polynomial. With allowance made for these relationships, from formulas (29), we obtain

$$N \overline{\delta G^2} = \Delta_D(S, t) = 3(1 - S - t)/4. \tag{31}$$

As can be seen from Fig. 4, this quantity increases only slightly with an increase in t and remains finite at $t = t_1 = 0.2228$ and $S_1 = 0.3236$, whereas the derivative $d\overline{\delta G^2}/dt$ diverges at this point. Upon the N–I transition, the quantity $N \overline{\delta G^2}$ jumpwise increases from 0.2631 to a value of 3/5, which is independent of temperature. The temperature dependences of the fluctuations

$$\overline{\delta S^2} = \frac{t\Delta_P}{N(t - \Delta_P)} \tag{32}$$

in the nematic and isotropic phases are asymmetric with respect to T_{NI}. In the isotropic phase, we have $\overline{\delta S^2} \sim (T - T^*)^{-1}$ in the vicinity of the temperature T_{NI} and the value of $\overline{\delta S^2}$ approaches $1/(5N)$ at $t \gg \Delta_P = 1/5$. In the nematic phase, we obtain

$$\Delta_P(S, t) = (1 + S - 2S^2 - 3t)/2 \tag{33}$$

and $\overline{\delta S^2}$ more rapidly decreases away from the temperature T_{NI}. This is in qualitative agreement with the experimental data on the temperature dependence of the longitudinal susceptibility for the nematic phase $\chi \sim \overline{\delta S^2}$ [17, 29]. The value of $N\overline{\delta S^2}$ for both phases at $T = T_{NI}$ is considerably larger than $N\overline{\delta G^2}$ and decreases from 2.1991 to 2.1812 upon the N–I transition.

From analyzing the results obtained for the uniaxial molecules, it is clearly seen that the calculation of the fluctuations $\overline{\delta S^2}$ with the use of ΔF_e [defined by expression (12)] instead of ΔF given by formula (8) (as was done in [14]) leads to the relationship

$$\overline{\delta S^2} = \frac{kT}{N}\left(\frac{\partial^2 F_e}{\partial S^2}\right)^{-1}_{S = S_e} = \frac{t^2}{N(t - \Delta_P)}. \tag{34}$$

This relationship differs from expression (32) and gives correct parameters $\overline{\delta S^2}$ only at $t \approx \Delta_P$, which corresponds to the temperatures $t \approx t^*$ ($t \approx t_1$) that cannot be experimentally obtained in the isotropic (nematic) phase. Even at $t = t_{NI}$, from formula (34), we obtain $N\overline{\delta S^2} = 2.4202$ and 2.4010 for the nematic and isotropic phases, respectively. These values differ significantly from the above values calculated from expression (32). In view of the difference between formulas (32) and (34), expression (32) can be derived without recourse to relationship (8) (see Appendix 2).

4.2. Biaxial Molecules

At $\lambda_1 \neq 0$ and a fixed ratio T/T_{NI}, the quantities $\overline{\delta S^2}$ and $\overline{\delta G^2}$ increase with an increase in λ_1 due to a decrease in the two-phase region $T_1 - T^*$. In this case, jumps in $\overline{\delta S^2}$ and $\overline{\delta G^2}$ at $T = T_{NI}$ increase in magnitude. The specific features of the dependence $G(T)$ considerably affect the temperature dependences of the fluctuations $\overline{\delta G^2}$ and $\overline{\delta S \delta G}$. In the nematic phase, at $t = t_2$ and under condition (24), from relationships (29), we obtain

$$N \overline{\delta G^2} = \Delta_D(\lambda_1, t_2), \quad \overline{\delta S \delta G} = -\lambda_1 \overline{\delta G^2}. \tag{35}$$

As a result, we have $\overline{\delta S \delta G} < 0$ in the range $0 < t \leq t_2$ regardless of the value of λ_1. At $t > t_2$ and $\partial G/\partial T < 0$, the values of $\overline{\delta G^2}$ and $\overline{\delta S \delta G}$ increase rapidly. The numerator in formula (29) for $\overline{\delta S \delta G}$ involves two terms with different signs and becomes zero under the condition

$$t\Delta_{PD} = -\lambda_1 J. \tag{36}$$

For fixed λ_1, the solution to the system of equations (13) and (36) gives the quantities $t_3(\lambda_1)$, $S_3 = S_e(t_3, \lambda_1)$, and $G_3 = G_e(t_3, \lambda_1)$ corresponding to the equality $\overline{\delta S \delta G} = 0$. The dependences of the quantities t_3, S_3, and G_3 on λ_1 are represented in Figs. 2 and 3. It can be seen from Fig. 2 that, at $\lambda_1 \leq 0.111$, the inequality $t_{NI}(\lambda_1) \leq t_3(\lambda_1)$ is satisfied and $\overline{\delta S \delta G} < 0$ over the entire range $t < t_{NI}$ (curve 2'' in the inset in Fig. 4). In the range $0.075 < \lambda_1 < 0.111$, the inequality $\overline{\delta S \delta G} < 0$ is valid and the function $G(t)$ decreases with an increase in $t > t_2(\lambda_1)$.

At $\lambda_1 > 0.111$, the values of $\overline{\delta S \delta G}$ are positive in the vicinity of T_{NI}. The dependence $S_3(\lambda_1)$ is weak, whereas the dependence $G_3(\lambda_1)$ exhibits a nearly linear behavior and is very similar to the dependence $G_2(\lambda_1)$.

From formulas (29), it follows that, in the case when the condition

$$t(\Delta_D - \Delta_{PD}) = J(1 + \lambda_1) \qquad (37)$$

is satisfied, the equality $\overline{\delta S \delta G} = \overline{(\delta G)^2}$ holds. In the nematic phase, at fixed λ_1, the solution of the system of equations (13) and (37) leads to the dependences $t_4(\lambda_1)$, $S_4 = S_e(t_4, \lambda_1)$, and $G_4 = G_e(t_4, \lambda_1)$, which are shown in Figs. 2 and 3. It can be seen from Fig. 2 that, in the nematic phase, at $\lambda_1 < 0.184$ and $T = T_{NI}$, we have $\overline{\delta S \delta G}(T_{NI}) < \overline{\delta G^2}(T_{NI})$. This situation is illustrated by curves 3' and 3" in Fig. 4. As can be seen from Fig. 3, the dependence $S_4(\lambda_1)$ is nonmonotonic and differs significantly from the dependences $S_{2,3}(\lambda_1)$. On the other hand, the dependence $G_4(\lambda_1)$ exhibits a nearly linear behavior and differs from the dependences $G_{2,3}(\lambda_1)$ only at $\lambda_1 \leq 1/3$.

For the isotropic phase, Eq. (37) has the solution

$$t_5 = (1 + \lambda_1)/5. \qquad (38)$$

The corresponding dependence is plotted in Fig. 2. The inequality $\overline{\delta S \delta G}(T_{NI}) < \overline{\delta G^2}(T_{NI})$ holds at $\lambda_1 < 0.122$. At $\lambda_1 > 0.184$, the inequality $\overline{\delta S \delta G}(T_{NI}) > \overline{\delta G^2}(T_{NI})$ is satisfied for both phases (see Fig. 4). In the isotropic phase, relationships (29) are reduced to the following formulas:

$$N\overline{\delta S^2} = \frac{5t - 3\lambda_1^2}{25[t - t^*(\lambda_1)]}, \quad N\overline{\delta G^2} = \frac{3(5t - 1)}{25[t - t^*(\lambda_1)]},$$

$$N\overline{\delta S \delta G} = \frac{3\lambda_1}{25[t - t^*(\lambda_1)]}, \qquad (39)$$

where $t^*(\lambda_1)$ is given by expression (22). Then, at $t \approx t^*(\lambda_1)$ and $N\overline{\delta G^2} \gg 3/5$, we obtain

$$N\overline{\delta S^2} = \frac{1}{25[t - t^*(\lambda_1)]}, \quad \overline{\delta G^2} = 9\lambda_1^2 \overline{\delta S^2},$$

$$\overline{\delta S \delta G} = 3\lambda_1 \overline{\delta S^2}. \qquad (40)$$

Note that the last two formulas directly follow from relationship (A1.5) [valid in the vicinity of $t \approx t^*(\lambda_1)$] and the expression $\delta G = (dG/dS)_{S_e = 0}\delta S = 3\lambda_1 \delta S$. In this temperature range, the inequalities $\overline{\delta G^2} \leq \overline{\delta S \delta G} \leq \overline{\delta S^2}$ are satisfied at $\lambda_1 \leq 1/3$. As the difference $[t - t^*(\lambda_1)]$ increases, the quantities $N\overline{\delta S^2}$ and $N\overline{\delta G^2}$

approach their limiting values of 1/5 and 3/5 and the quantity $\overline{\delta S \delta G} \sim [t - t^*(\lambda_1)]^{-1}$ tends to zero. A comparison of formulas (39) and (32) at $\Delta_P(S = 0) = 1/5$ indicates that, at a fixed difference $t - t^*$, the molecular biaxiality leads only to a small decrease in the value of $\overline{\delta S^2}$, whereas the temperature dependences of the quantities $\overline{\delta G^2}$ and $\overline{\delta S \delta G}$ and their divergence at $t = t^*(\lambda_1)$ in the isotropic phase are completely determined by the molecular biaxiality.

The fluctuation effects in the nematic and isotropic phases in the vicinity of the N–I transition differ considerably in character. In the nematic phase, at $\lambda_1 = 0.2$ and $T = T_{NI}$, the values of $N\overline{\delta S^2}$, $N\overline{\delta G^2}$, and $N\overline{\delta S \delta G}$ are equal to 5.7214, 0.4431, and 0.6272, respectively. As a result, we obtain the inequalities $\overline{\delta S^2} \gg \overline{\delta G^2}$ and $\overline{\delta S^2} \gg \overline{\delta S \delta G}$. At $\lambda_1 < 0.2$, an increase in $\overline{\delta S^2}$ in the vicinity of T_{NI} due to molecular biaxiality is not large enough to change the inequality

$$\overline{(\delta S)_V^2} \ll S^2, \qquad (41)$$

which follows from the experimental data for typical calamitic nematic liquid crystals, such as MBBA and alkylcyanobiphenyls [17, 29]. In inequality (41), $\overline{(\delta S)_V^2}$ is the homogeneous long-wavelength fluctuation of S in the volume $V = 4\pi\xi^3/3$, where ξ is the correlation length of fluctuations of S. By virtue of inequality (41), the effect of fluctuations of S and G on the physical properties dependent on S is weak in the calamitic nematic phase of typical mesogenic compounds. On the other hand, condition (41) is the criterion for the applicability of the mean-field approach to the description of the N–I transition [28]. For mesogenic compounds with parameters λ_1 close to 1/3, condition (41) is violated and the values of $\overline{\delta G^2}$ and $\overline{\delta S \delta G}$ become comparable to those of $\overline{\delta S^2}$. In this case, the N–I transition should be described taking into account the fluctuations $\overline{\delta G^2}$ and $\overline{\delta S \delta G}$ in addition to the fluctuations $\overline{\delta S^2}$.

In the isotropic phase, at the transition point T_{NI}, the values of $N\overline{\delta S^2}$, $N\overline{\delta G^2}$, and $N\overline{\delta S \delta G}$ (even at $\lambda_1 = 0.2$) are equal to 4.9059, 2.2941, and 2.8235, respectively; i.e., they are close in order of magnitude. Therefore, the pretransitional effects should be analyzed with due regard for the fluctuations $\overline{\delta S^2}$, $\overline{\delta G^2}$, and $\overline{\delta S \delta G}$. This is particularly true for the description of the response of nematic liquid crystals to external actions.

5. RESPONSE OF A NEMATIC LIQUID CRYSTAL TO EXTERNAL FIELDS

Let us consider the response of a calamitic nematic liquid crystal to an external field h, which leads to a change in the order parameters S and G at a fixed orientation of the director $\mathbf{n}$. The susceptibilities serve as a measure of the linear response and are defined by the relationships

$$\chi_S = (\partial S/\partial h)_{T;\,h\to 0}, \quad \chi_G = (\partial G/\partial h)_{T;\,h\to 0}. \quad (42)$$

For magnetic (H) and high-frequency electric [$E(\omega)$] fields parallel to the director, the expressions for h have the form

$$h_H = \frac{\Delta k}{3}H^2, \quad h_E = \frac{\Delta\gamma(\omega)f_\|(\omega)}{3}E^2(\omega), \quad (43)$$

where $\Delta k = k_{zz} - (k_{xx} + k_{yy})/2$ and $\Delta\gamma(\omega) = \gamma_{zz}(\omega) - [\gamma_{xx}(\omega) + \gamma_{yy}(\omega)]/2$ are the anisotropies of the diamagnetic and electric molecular polarizabilities, respectively; $f_\|(\omega)$ is the component of the tensor of the local field acting on a molecule in the liquid crystal; and $E(\omega)$ is the amplitude of the macroscopic electric field in the liquid crystal. In the presence of the field h, formula (8) takes the form

$$\Delta F = -\frac{u}{2}(S + \lambda_1 G)^2 - h(S + \lambda_2 G)$$
$$+ kT[\lambda_P S + \lambda_D G - \ln Z(\lambda_P, \lambda_D)]. \quad (44)$$

Here, the second term on the right-hand side characterizes the energy of interaction between the liquid crystal and the field per molecule and the parameter λ_2 is defined by expression (7), in which γ_{ii} is replaced either by k_{ii} at $h = h_H$ or by $\gamma_{ii}(\omega)$ at $h = h_E$. In the general case, the values of λ_1 and λ_2 are different, even though they can coincide for particular compounds. The parameters $\lambda_P(S, G)$ and $\lambda_D(S, G)$ are determined from the system of equations (4), in which $S = S(h)$ and $G = G(h)$. Under thermodynamic equilibrium conditions $(\partial F/\partial S)_{T,h} = (\partial F/\partial G)_{T,h} = 0$, with the use of relationships (44), we obtain the system of equations of state for a nematic liquid crystal in the external field h, that is,

$$\lambda_P(S, G) = \frac{u}{kT}(S + \lambda_1 G) + \frac{h}{kT},$$
$$\lambda_D(S, G) = \frac{u\lambda_1}{kT}(S + \lambda_1 G) + \frac{\lambda_2 h}{kT}. \quad (45)$$

Substitution of these expressions into formula (3) gives the equilibrium distribution function of molecules in the presence of the external field:

$$f_{e,h}(\Omega) = \frac{1}{8\pi^2 Z_{e,h}}$$
$$\times \exp\left[\frac{u}{kT}(S + \lambda_1 G)(P_2 + \lambda_1 D) + \frac{h}{kT}(P_2 + \lambda_2 D)\right],$$

$$Z_{e,h} = \frac{1}{8\pi^2} \quad (46)$$

$$\times \int \exp\left[\frac{u}{kT}(S + \lambda_1 G)(P_2 + \lambda_1 D) + \frac{h}{kT}(P_2 + \lambda_2 D)\right] d\Omega.$$

Differentiation of the equations of state (45) with respect to h at a constant temperature with allowance made for expressions (18) leads to the system of equations in $(\partial S/\partial h)_T$ and $(\partial G/\partial h)_T$. By solving this system, we obtain

$$\left(\frac{\partial S}{\partial h}\right)_T = \frac{1}{kT(t - \Delta_A)}[t\Delta_P - \lambda_1^2 J + \lambda_2(t\Delta_{PD} + \lambda_1 J)],$$

$$\left(\frac{\partial G}{\partial h}\right)_T = \frac{1}{kT(t - \Delta_A)}[t\Delta_{PD} + \lambda_1 J + \lambda_2(t\Delta_D - J)]. \quad (47)$$

Here, the parameters described by formulas (15), (17), and (21) are calculated with the distribution function (46) and depend on h. The derivatives $(\partial S/\partial h)_T$ and $(\partial G/\partial h)_T$ diverge at the temperatures $t^*(\lambda_1, h)$ and $t_1(\lambda_1, h)$ obeying the equation

$$t = \Delta_A(h). \quad (48)$$

The parameter Δ_A [expression (21)] is the second-order cumulant, which can be written in the following form:

$$\Delta_A(h) = \frac{\partial^2 \ln Z_{e,h}}{\partial \lambda_A^2} = \langle A|A\rangle, \quad (49)$$

where $\lambda_A = u(S + \lambda_1 G)/kT$. The dependence $\Delta_A(h)$ can be represented as a series:

$$\Delta_A(h) = \sum_{n=0}^{\infty} \frac{\lambda_B^n}{n!}\left(\frac{\partial^{2+n}\ln Z_{e,h}}{\partial\lambda_A^2 \partial\lambda_B^n}\right)_{\lambda_B = 0}$$

$$\equiv \sum_{n=0}^{\infty} \frac{\lambda_B^n}{n!}\langle A|A|\overbrace{B|\ldots|B}^{n}\rangle_0, \quad (50)$$

where $\lambda_B = h/kT$ and $B = P_2 + \lambda_2 D$. Here, all the cumulant averages $\langle a_1|a_2|\ldots|a_n\rangle_0$ are calculated at $h = 0$ with the distribution function (11). In the approximation linear in h, Eq. (48) for the isotropic phase takes the form

$$T^* = \frac{u}{5k}(1 + 3\lambda_1^2)\left\{1 + \frac{2[1 - 3\lambda_1(\lambda_1 + 2\lambda_2)]}{7kT^*(1 + 3\lambda_1^2)}h\right\}. \quad (51)$$

For uniaxial molecules at $\lambda_1 = \lambda_2 = 0$, with due regard for expressions (43) at $h = h_H$, this expression coincides

with the relationship obtained earlier in [30] in a different way. At $\lambda_1 = \lambda_2 = 1/3$, T^* becomes independent of h.

In the limit $h \longrightarrow 0$, the rearrangement of relationships (47) with allowance made for expressions (29) permits us to obtain susceptibilities (42) in the following form:

$$\chi_S = \frac{N}{kT}[\overline{\delta S^2} + \lambda_2 \overline{\delta S \delta G}],$$
$$\chi_G = \frac{N}{kT}[\overline{\delta S \delta G} + \lambda_2 \overline{\delta G^2}]. \tag{52}$$

A comparison of formulas (23) and (47) at $h = 0$ makes it possible to derive the relationships between the susceptibilities and the temperature dependences of the order parameters S and G in the absence of a field. At $\lambda_1 = \lambda_2$, these relationships are simplified and take the form

$$\chi_S = -\frac{T}{u(S + \lambda_1 G)}\frac{\partial S}{\partial T}, \quad \chi_G = -\frac{T}{u(S + \lambda_1 G)}\frac{\partial G}{\partial T}. \tag{53}$$

From these relationships, we have $\chi_G < 0$ at $t < t_2$ and $\partial G/\partial T > 0$. The contributions of the fluctuations $\overline{\delta S \delta G}$ to the susceptibility χ_S and the fluctuations $\overline{\delta G^2}$ to the susceptibility χ_G are determined by the value of λ_2, which is different for the electric and magnetic fields. At $t = t_3$ and $\overline{\delta S \delta G} = 0$, the susceptibilities χ_S and χ_G are governed only by the fluctuations $\overline{\delta S^2}$ and $\overline{\delta G^2}$, respectively.

In the isotropic phase, substitution of expressions (39) into formulas (52) gives

$$\chi_S^{(i)} = \frac{5t - 3\lambda_1(\lambda_1 - \lambda_2)}{25kT[t - t^*(\lambda_1)]},$$
$$\chi_G^{(i)} = \frac{3(5t\lambda_2 + \lambda_1 - \lambda_2)}{5t - 3\lambda_1(\lambda_1 - \lambda_2)}\chi_S^{(i)}. \tag{54}$$

Since $5t > 1$ and $\lambda_1 - \lambda_2 \ll 1$, from formulas (54), we find

$$\chi_G^{(i)} = 3\lambda_2\chi_S^{(i)}\left[1 + \frac{1}{5t\lambda_2}(\lambda_1 - \lambda_2)(1 + 3\lambda_1\lambda_2)\right] \approx \tag{55}$$
$$3\lambda_2\chi_S^{(i)}.$$

In the linear-field approximation, the order parameters $S(h)$ and $G(h)$ induced by the field h in the isotropic phase of the nematic liquid crystal are given by the expressions

$$S(h) = \chi_S^{(i)}h, \quad G(h) = \chi_G^{(i)}h = 3\lambda_2 S(h). \tag{56}$$

The parameters $S(h)$ and $G(h)$ increase proportionally to $[T - T^*(\lambda_1)]^{-1}$ as the temperature T_{NI} is approached. Making allowance for formulas (43) and (54), expressions (56) fit the experimental data obtained in [19–21]

for pure nematic liquid crystals fairly well. The interpretation of the dependences $G(h) \sim S(h) \sim (T - T^*)^{-1}$ observed in the constant field h for the order parameters of impurity biaxial molecules with a small concentration in the isotropic phase of the nematic matrix [21] calls for special examination, because the constant λ_m in the expression $G(h) = 3\lambda_m S(h)$ in this case is predominantly determined by the interaction between the impurity and the matrix.

Now, we analyze the possibilities of using formulas (56) to interpret the experimental data on the quadrupole splitting $\Delta \nu_k$ of the ^{2}D NMR lines associated with the C–D$_k$ bonds. The quadrupole splitting $\Delta \nu_k$ depends on the orientation of the C–D$_k$ bond with respect to the axes of the molecular coordinate system xyz and orientational order of molecules and can be represented as

$$\Delta \nu_k = \text{const}(SS_\beta + GG_{\beta\varphi}/3). \tag{57}$$

Here, $S_\beta = (3\cos^2\beta - 1)/2$, $G_{\beta\varphi} = (3/2)\sin^2\beta\cos 2\varphi$ β is the angle between the C–D$_k$ bond and the z axis of the molecular coordinate system xyz, and φ is the angle between the x axis and the projection of the C–D$_k$ bond onto the xy plane. The quadrupole splitting $\Delta \nu_k$ can become zero for a continuum of C–D$_k$ directions. In the molecular coordinate system, the equation $\Delta \nu_k = 0$ can be rearranged to the following form:

$$x^2 S_{xx} + y^2 S_{yy} + z^2 S_{zz} = 0. \tag{58}$$

Among the three parameters S_{ii}, two parameters have the same sign. By designating their magnitudes as S_u and S_v and allowing for the condition $\text{Tr}\mathbf{S} = 0$, from Eq. (58), we obtain the expression

$$\bar{u}^2 S_u + \bar{v}^2 S_v - \bar{w}^2(S_u + S_v) = 0, \tag{59}$$

which is an equation of an elliptic cone with a vertex at the origin of the coordinates and the axis $\bar{w}$. In the section that is perpendicular to the $\bar{w}$ axis and is located at the distance $c = \pm(S_u + S_v)^{-1/2}$ from the origin of the coordinates, the cone directrix is an ellipse with the semiaxes $a = (S_u)^{-1/2}$ and $b = (S_v)^{-1/2}$. The angles β_u and β_v determining the half-aperture of the cone are defined as

$$\beta_u = \arctan(1 + S_v/S_u)^{1/2},$$
$$\beta_v = \arctan(1 + S_u/S_v)^{1/2}. \tag{60}$$

The equality $\Delta \nu_k = 0$ is satisfied for all the C–D$_k$ directions lying on this "magic" cone $C(xyz)$. The diagonals $|\bar{u}| = |\bar{v}| = |\bar{w}|$ of the molecular coordinate system lie on the cone $C(xyz)$ and correspond to $S_\beta = G_{\beta\varphi} = 0$. For uniaxial molecules with the axis $z = \bar{w}$ and $S_u = S_v$, the circular cone $C(xyz)$ is characterized by the half-aperture angle $\beta \approx 54.74°$.

The shape of the cone $C(xyz)$ is specified by the parameters S and G and depends on the mesophase temperature and the ratio between the parameters S_u and S_v. At $S > G$ and $S_{xx} = -(S - G)/2$, $S_{yy} = -(S + G)/2$, and $S_{zz} = S$, we have $\bar{u} = x$, $\bar{v} = y$, $\bar{w} = z$. In the nematic phase, at values of λ_1 close to $1/3$, the parameters S and G in the vicinity of the N–I transition are small and are related by the expression $S = 3\lambda_1 G$ [see relationship (A1.5)]. Therefore, the angles

$$\beta_x = \arctan\left(\frac{2}{1 - 3\lambda_1}\right)^{1/2}, \quad \beta_y = \arctan\left(\frac{2}{1 + 3\lambda_1}\right)^{1/2} \quad (61)$$

are independent the temperature. As the value of λ_1 approaches $1/3$, the semiaxis a increases and tends to infinity at $G = S$. In this case, the cone $C(xyz)$ degenerates into two mutually perpendicular planes which intersect along the x axis and make the angles $\beta_y = \pm 45°$ with the z axis. For particular compounds and C–D$_k$ bonds, one of the parameters S_{ii} in Eq. (58) can change sign with a variation in the mesophase temperature, because the dependence $G(S)$ in the nematic phase exhibits a nonmonotonic behavior. As a consequence, the $\bar{w}$ axis changes its direction from one axis in the system xyz to another axis. The changeover to the inequality $G > S$, which is valid only for biaxial impurity molecules in the calamitic nematic liquid crystal, is accompanied by the transformation of the above planes into the cone $C(xyz)$ with the axes $\bar{u} = x$, $\bar{v} = z$, and $\bar{w} = y$ and the semiaxes of the ellipse $a \gg b$.

In the isotropic phase, when expressions (56) hold true, λ_1 in formulas (61) should be replaced by λ_2 or λ_m for impurity molecules) and the angles $\beta_{x, y}$ do not depend on the parameters $S(h)$ and $G(h)$. This circumstance accounts for the situation where the proportional relationship $\Delta\nu_k \sim S(h)$ is observed for a number of C–D$_k$ bonds in the molecule, whereas the other C–D$_k$ bonds in the same molecule are characterized by $\Delta\nu_n = 0$ [19, 21]. The orientation of the latter bonds is similar to that of the directrix of the cone $C(xyz)$ with parameters (61). This provides the basis for the technique of determining the orientation of C–D$_k$ bonds in the molecular coordinate system.

6. CONCLUSIONS

Thus, the results obtained in the present work demonstrated that the molecular biaxiality substantially affects the dependences $S(T)$ and $G(T)$ and the magnitudes S_{NI} and G_{NI} upon the N–I transition. An increase in the molecular biaxiality parameter λ_1 is attended by a decrease in the values S_{NI} and G_{NI} and a narrowing of the two-phase region. However, the ratio $(T_{NI} - T^*)/(T_1 - T_{NI})$ remains unchanged up to the parameter $\lambda_1 = 1/3$, which is a limiting value for calamitic nematic liquid crystals and corresponds to the I–N$_b$ transition to

the biaxial nematic phase. The specific features of the dependence $G(T)$ have a considerable effect on the magnitude and temperature behavior of the fluctuations $\overline{\delta G^2}$ and $\overline{\delta S \delta G}$. The fluctuations $\overline{\delta S \delta G}$ in the nematic phase vary nonmonotonically and can change sign from negative to positive as the temperature T_{NI} is approached. In the nematic phase, the fluctuations $\overline{\delta G^2}$ and $\overline{\delta S \delta G}$ at values $\lambda_1 < 0.2$ typical of mesogenic molecules are appreciably less than the fluctuations $\overline{\delta S^2}$ and do not affect the applicability of the mean-field approach to the description of the N–I transition. At values of λ_1 close to $1/3$ and small parameters S_{NI}, the fluctuations $\overline{\delta S^2}$, $\overline{\delta G^2}$, and $\overline{\delta S \delta G}$ are large and comparable to each other, so that the mean-field approximation is inapplicable.

In the isotropic phase, the molecular biaxiality determines the ratios between the fluctuations $\overline{\delta S^2}$, $\overline{\delta G^2}$, and $\overline{\delta S \delta G}$ and their temperature behavior. At $\lambda_1 \approx 0.2$ for real mesogenic molecules, the fluctuations $\overline{\delta S^2}$, $\overline{\delta G^2}$, and $\overline{\delta S \delta G}$ are comparable to each other in the vicinity of the temperature T_{NI}. The inclusion of the molecular biaxiality makes it possible to explain the dependences $G(h) \sim S(h) \sim (T - T^*)^{-1}$, which are experimentally observed for the parameters $G(h)$ and $S(h)$ that are induced by the field h in the isotropic phase of the nematic. Moreover, the specific features of the quadrupole splitting of the NMR lines in the spectra of selectively deuterated mesogenic and impurity molecules in the isotropic phase of nematic liquid crystals can also be interpreted in terms of the molecular biaxiality.

APPENDIX 1

Let us now demonstrate that the expansions of ΔF [defined by formula (8)] and ΔF_e [represented by formula (12)] into a Landau series in powers of the parameters S and G up to fourth-order terms differ significantly. The expansion of the function $Z(\lambda_P, \lambda_D)$ [given by expression (3)] into a power series of $\lambda_{P, D}$ and substitution of this series into relationships (4) give the series $S = S(\lambda_P, \lambda_D)$ and $G = G(\lambda_P, \lambda_D)$ whose inversion makes it possible to obtain the dependences $\lambda_P(S, G)$ and $\lambda_D(S, G)$. With the required precision up to third-order terms, these dependences have the form

$$\lambda_P = 5S - \frac{25}{7}S^2 + \frac{25}{21}G^2 + \frac{425}{49}S^3 + \frac{425}{147}SG^2,$$

$$\lambda_D = \frac{5}{3}G\left(1 + \frac{10}{7}S + \frac{85}{49}S^2\right) + \frac{425}{441}G^3. \quad (A1.1)$$

The dependence $\lambda_P(S, G)$ is the even function and the dependence $\lambda_D(S, G)$ is the odd function of the parameter G. Substitution of formulas (A1.1) into the series $\ln Z(\lambda_P, \lambda_D)$ gives

$$\ln Z = \frac{5}{6}(3S^2 + G^2) - \frac{50}{21}(S^3 - SG^2)$$
$$+ \frac{425}{588}(3S^2 + G^2)^2. \tag{A1.2}$$

This expansion is a power series of the invariants $I_2 = \text{Tr}(\mathbf{S}^2) = (3S^2 + G^2)/2$ and $I_3 = \text{Tr}(\mathbf{S}^3) = 3(S^3 - SG^2)/4$ of the matrix $\mathbf{S}$ (1). In the diagonal form, this matrix has the following elements: $S_{xx} = -(S - G)/2$, $S_{yy} = -(S + G)/2$, and $S_{zz} = S$. Substitution of formulas (A1.1) and (A1.2) into relationship (8) leads to the sought expansion

$$\Delta F = -\frac{u}{2}(S + \lambda_1 G)^2 + \frac{5}{6}kT(3S^2 + G^2)$$
$$- \frac{25}{21}kT(S^3 - SG^2) + \frac{425}{1764}kT(3S^2 + G^2)^2. \tag{A1.3}$$

The minimization of expression (A1.3) with respect to the parameters S and G results in the system of equations (10). From this system of equations, we derive the relationship

$$\lambda_D(S, G) = \lambda_1 \lambda_P(S, G). \tag{A1.4}$$

Substitution of series (A1.1) into relationship (A1.4) gives the expression

$$G = 3\lambda_1 S - \frac{45}{7}\lambda_1(1 - \lambda_1^2)S^2 + \ldots. \tag{A1.5}$$

With this expression, the function ΔF described by formula (A1.3) can be reduced to a form $\Delta F(S)$ with coefficients dependent on λ_1. At $G < S$, the third-order term in formula (A1.3) is negative and the N–I transition is a first-order transition. Let us consider the situation at $G \leq S$ when the N–I transition is similar in character to a continuous transition and the parameters S and G are small in its vicinity. Then, in relationship (A1.5), it is possible to retain only the first term. Its substitution into formula (A1.3) leads to the series

$$\Delta F(S) = \frac{1}{2}a(T - T^*)S^2 - \frac{1}{3}bS^3 + \frac{1}{4}cS^4 \tag{A1.6}$$

with the coefficients

$$a(\lambda_1) = 5k(1 + 3\lambda_1^2), \quad b(\lambda_1, T) = \frac{25}{7}kT(1 - 9\lambda_1^2),$$
$$\tag{A1.7}$$
$$c(\lambda_1, T) = \frac{425}{49}kT(1 + 3\lambda_1^2)^2.$$

At $\lambda_1 = 0$, these coefficients are reduced to the coefficients (4.23) obtained in [27]. The coefficient $b(\lambda_1, T)$ becomes zero at $\lambda_1 = 1/3$, which agrees with the results following from formula (7). The limiting temperature

of the stability of the isotropic phase $t^* = kT^*/u$ and the parameter $S^* = S(t^*)$ are defined by the expressions

$$t^*(\lambda_1) = (1 + 3\lambda_1^2)/5, \quad S^* = \frac{7(1 - 9\lambda_1^2)}{17(1 + 3\lambda_1^2)^2}. \tag{A1.8}$$

The temperature t_{NI} of the N–I transition and the parameter S_{NI} can be written as follows:

$$t_{NI} = \frac{153(1 + 3\lambda_1^2)^3 t^*}{153(1 + 3\lambda_1^2)^3 - 10(1 - 9\lambda_1^2)^2}, \tag{A1.9}$$
$$S_{NI} = 2S^*/3.$$

The limiting temperature of the stability of the nematic phase t_1 and the parameter $S_1 = S(t_1)$ are related to parameters (A1.8) through the expression

$$t_1 = \frac{68(1 + 3\lambda_1^2)^3 t^*}{68(1 + 3\lambda_1^2)^3 - 5(1 - 9\lambda_1^2)^2}, \tag{A1.10}$$
$$S_1 = S^*/2.$$

In the λ_1 range under consideration, the ratios between the parameters S^*, S_{NI}, and S_1 do not depend on λ_1 and the two-phase region $t_1 - t^*$ decreases with an increase in λ_1. However, the ratio $(t_{NI} - t^*)/(t_1 - t_{NI})$ varies from 7.4 at $\lambda_1 = 0$ to 8 in the limit $\lambda_1 = 1/3$.

Now, expansions similar to those represented by formulas (A1.3) and (A1.6) will be derived for the function ΔF_e given by formula (12). Let us introduce the following designations:

$$\eta = S + \lambda_1 G,$$
$$A(\theta, \psi) = P_2(\cos\theta) + \lambda_1 D(\theta, \psi). \tag{A1.11}$$

It can be shown that the two equations $(\partial F_e/\partial S)_T = (\partial F_e/\partial G)_T = 0$ are equivalent to one self-consistent equation for the parameter η; that is,

$$\eta = \langle A \rangle_e \equiv \int A(\theta, \psi) f_e(\Omega) d\Omega. \tag{A1.12}$$

The expansion of the function ΔF_e [formula (12)] in powers of η has the form

$$\Delta F_e(\eta) = \frac{u}{2T}[T - T^*(\lambda_1)]\eta^2$$
$$- \frac{(1 - 9\lambda_1^2)u^3}{105(kT)^2}\eta^3 + \frac{(1 + 3\lambda_1^2)^2 u^4}{700(kT)^3}\eta^4 + \ldots, \tag{A1.13}$$

where the expression for $T^*(\lambda_1) = u(1 + 3\lambda_1^2)/5k$ coincides with that in relationship (A1.8). Substitution of the first term of expansion (A1.5) into formula (A1.13)

gives the expansion of $\Delta F_e(S)$ in the form of series (A1.6) with the coefficients

$$a_e(\lambda_1, T) = \frac{u}{T}(1 + 3\lambda_1^2)^2,$$

$$b_e(\lambda_1, T) = \frac{(1 - 9\lambda_1^2)(1 + 3\lambda_1^2)^3 u^3}{35(kT)^2}, \qquad \text{(A1.14)}$$

$$c_e(\lambda_1, T) = \frac{(1 + 3\lambda_1^2)^6 u^4}{175(kT)^3}.$$

These coefficients differ from coefficients (A1.7) and, at $\lambda_1 = 0$, coincide with those given in [2, 26]. At $T = T^*(\lambda_1)$, we have $a_e = a$, $b_e = b$, and $c_e = 7c/17$. Therefore, the use of expansion (A1.13) is sufficiently correct only in the isotropic phase at temperatures close to $T^*(\lambda_1)$.

APPENDIX 2

For a nematic liquid crystal with uniaxial molecules at a constant volume, formula (32) can be obtained from the general thermodynamic relations [28]

$$\overline{\delta S^2} = \left(\frac{\partial S}{\partial T}\right)^2_{V; \, \delta T = 0} \overline{\delta T^2}, \quad \overline{\delta T^2} = \frac{kT^2}{C_V} \qquad \text{(A2.1)}$$

under the assumption that the temperature fluctuations are responsible for the fluctuations of $S(T)$. The heat capacity at a constant volume with due regard for expression (6) at $\lambda_1 = 0$ can be written in the form

$$C_V = \left[N\frac{\partial E(S)}{\partial T}\right]_V = -NuS\left(\frac{\partial S}{\partial T}\right)_V. \qquad \text{(A2.2)}$$

Substitution of formula (A2.2) into relations (A2.1) gives the relationship

$$\overline{\delta S^2} = -\frac{kT^2}{Nu}\left(\frac{\partial \ln S}{\partial T}\right)_V \qquad \text{(A2.3)}$$

between the fluctuations $\overline{\delta S^2}$ in the nematic phase and the dependence $S(T)$. By substituting the first expression out of the two expressions in (23) at $\lambda_1 = 0$ into relationship (A2.3), we obtain formula (32).

REFERENCES

1. P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Clarendon, Oxford, 1993; Mir, Moscow, 1982).
2. M. J. Freiser, Mol. Cryst. Liq. Cryst. **14** (1–2), 165 (1971).
3. J. P. Straley, Phys. Rev. A **10** (5), 1881 (1974).
4. R. G. Priest, Solid State Commun. **17** (4), 519 (1975).
5. G. R. Luckhurst, C. Zannoni, P. L. Nordio, and U. Segre, Mol. Phys. **30** (5), 1345 (1975).
6. W. M. Gelbart and B. Barboy, Mol. Cryst. Liq. Cryst. **55** (1–2), 209 (1979).
7. N. P. Tumanyan and E. P. Sokolova, Zh. Fiz. Khim. **58** (10), 2444 (1984).
8. B. Bergersen, P. Palffy-Muhoray, and D. A. Dunmur, Liq. Cryst. **3** (3), 347 (1988).
9. B. Mulder, Phys. Rev. A **39** (1), 360 (1989).
10. B. Tjipto-Margo and G. T. Evans, J. Chem. Phys. **94** (6), 4546 (1990).
11. A. Ferrarini, G. Moro, P. L. Nordio, and G. R. Luckhurst, Mol. Phys. **77** (1), 1 (1992).
12. E. F. Gramsbergen, L. Longa, and W. H. De Jeu, Phys. Rep. **135** (2), 195 (1986).
13. Z. H. Wang and P. H. Keyes, Phys. Rev. E **54** (5), 5249 (1996).
14. R. Blinc, S. Lugomer, and B. Zeks, Phys. Rev. **9** (6), 2214 (1974).
15. Lin Lei, Phys. Rev. Lett. **43** (21), 1604 (1979).
16. B. Pouligny and J. Lalanne, Phys. Rev. A **26** (6), 3679 (1982).
17. E. M. Aver'yanov, Zh. Éksp. Teor. Fiz. **97** (3), 855 (1990) [Sov. Phys. JETP **70**, 479 (1990)].
18. E. M. Aver'yanov, Zh. Éksp. Teor. Fiz. **110** (5), 1820 (1996) [JETP **83**, 1000 (1996)].
19. G. S. Attard, P. A. Beckmann, J. W. Emsley, *et al.*, Mol. Phys. **45** (5), 1125 (1982).
20. J. W. Emsley, C. T. Imrie, G. R. Luckhurst, and R. D. Newmark, Mol. Phys. **63** (2), 317 (1988).
21. G. R. Luckhurst, J. Chem. Soc., Faraday Trans. 2 **84** (8), 961 (1988).
22. H. Haken, *Information and Self-Organization: A Macroscopic Approach to Complex Systems* (Springer-Verlag, Berlin, 1988; Mir, Moscow, 1991).
23. E. M. Aver'yanov and A. N. Primak, Liq. Cryst. **10** (4), 555 (1991).
24. E. M. Aver'yanov and A. N. Primak, Liq. Cryst. **13** (1), 139 (1993).
25. A. A. Gerasimov, Ukr. Fiz. Zh. **27** (9), 1314 (1982).
26. S. Chandrasekhar, *Liquid Crystals*, 2nd ed. (Cambridge Univ. Press, Cambridge, 1992; Mir, Moscow, 1980).
27. J. Katriel, G. F. Kventsel, G. R. Luckhurst, and T. J. Sluckin, Liq. Cryst. **1** (4), 337 (1986).
28. L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 3rd ed. (Nauka, Moscow, 1976; Pergamon, Oxford, 1980), Part 1.
29. E. M. Aver'yanov, *Local-Field Effects in Optics of Liquid Crystals* (Nauka, Novosibirsk, 1999).
30. P. Palffy-Muhoray and D. A. Dunmur, Mol. Cryst. Liq. Cryst. **97**, 337 (1983).

Translated by O. Borovik-Romanova