STATISTICAL THEORY OF THE THERMODYNAMIC AND STRUCTURAL
PROPERTIES OF NEMATIC LIQUID CRYSTALS WITH INTERMOLECULAR
CORRELATIONS TAKEN INTO ACCOUNT

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The characteristics of nematic liquid crystals are expressed in terms of
mean force potentials, which satisfy a nonlinear integral equation. This
equation is solved numerically and results are given for the nematic PAA.

Interest in liquid crystals results from the diversity of their physical properties
and from their wide application in practice [1-3]. Extensive experimental data have been
collected on the thermophysical, structural, and optical properties [4-6]. Theoretical
studies have been based mainly on the Maier—Saupe theory (see [1]) and on its modifica-
tions. This theory is a mean field approximation. In addition, computer simulations have
begun to play a larger role [7, 8].

The strong correlation of the angular variables, which is the distinguishing feature
of nematics, has stimulated the construction of theories which attempt to take into account
these correlations in an explicit way (see [9], for example). Correlation effects in
liquid crystals can be studied with the help of the statistical method of angular distribu-
tions [10], which was successfully used earlier in studying systems with rotational degrees
of freedom [11], and also the simplest molecular crystals with defects [12].

This approach is used in the present paper to develop a statistical theory of the
thermodynamic and structural properties of nematic liquid crystals. The theory allows one
to calculate the microscopic and macroscopic characteristics of nematics on a unified basis
without the use of adjustable parameters.

Statistical Description of Nematics. We consider a system of N molecules in a volume
V. Let the position of the center of mass of molecule i be given by the vector q_i and
its orientation by the vector ω_i. We divide the volume of the system V into N equal cells,
where the volume of each cell is $v = V/N$. Following [10], we use the sequence of partial
distribution functions $F_i(q_i, \omega_i)$, $F_{ij}(q_i, \omega_i, q_j, \omega_j)$, and so on, which are obtained by
integration of the Gibbs distribution function. These functions determine the probability
density of finding arbitrary particles near the points $q_i \in v_i$, $q_j \in v_j$ with orientations ω_i
and ω_j under the condition that all of the remaining cells contain one molecule each.
These functions satisfy the equations

$$\int_{v_i} dq_i \int_{\Omega_i} d\omega_i F_i(q_i, \omega_i) = 1, \tag{1}$$

$$F_i(q_i, \omega_i) = \int_{v_j} dq_j \int_{\Omega_j} d\omega_j F_{ij}(q_i, \omega_i, q_j, \omega_j), \tag{2}$$

where Ω is the volume element corresponding to the angular variables of the molecule. The
two-particle function is related to the three-particle function by an integral relation,
etc. Below we take into account the first two functions of the infinite hierarchy; this
corresponds to taking into account only pair correlations between molecules.

Using the concept of mean force potentials [10], the functions in (1) and (2) can be
written in the form

$$F_i(q_i, \omega_i) = Q^{-1} \exp\{-\beta\varphi_i(q_i, \omega_i)\}, \tag{3}$$
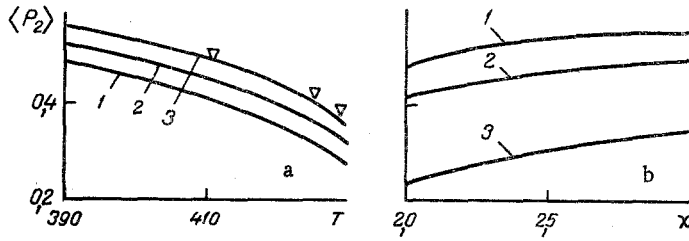
Fig. 1. (a) Dependence of the order parameter on temperature for $\chi = 2.0$ (curve 1); 2.5 (curve 2); 3.0 (curve 3), where the points are the experimental data of [20]. (b) Dependence of the order parameter on the ellipticity parameter for $\theta = k_B$, $T/\varepsilon_0 = 0.75$ (curve 1); 0.7885 (curve 2); 0.827 (curve 3). T, °K.

$$F_{ij}(\mathbf{q}_i, \; \omega_i, \; \mathbf{q}_j, \; \omega_j) = Q^{-2} \exp\{- \beta [\varPhi(\mathbf{q}_i, \; \omega_i, \; \mathbf{q}_j, \; \omega_j) + \varphi_{ij}(\mathbf{q}_i, \; \omega_i, \; \mathbf{q}_j, \; \omega_j)]\}, \tag{4}$$

where

$$Q = \int_{v_i} d\mathbf{q}_i \int_{\Omega_i} d\omega_i \exp\{- \beta\varphi_i(\mathbf{q}_i, \; \omega_i)\}; \tag{5}$$

$\varPhi$ is the interaction potential of two molecules, $\varphi_i(\mathbf{q}_i, \; \omega_i)$ and $\varphi_{ij}(\mathbf{q}_i, \; \omega_i, \mathbf{q}_j, \omega_j)$ are the mean force potential and mean torque potential, and are sums of the forms

$$\varphi_i(\mathbf{q}_i, \; \omega_i) = \sum_{j \neq i}^{N} \varphi_{i,j}(\mathbf{q}_i, \; \omega_i), \tag{6}$$

$$\varphi_{ij}(\mathbf{q}_i, \; \omega_i, \; \mathbf{q}_j, \; \omega_j) = \sum_{l \neq i,j}^{N} \varphi_{ij,l}(\mathbf{q}_i, \; \omega_i, \; \mathbf{q}_j, \; \omega_j). \tag{7}$$

The terms in the sum (6) are given by the expressions

$$\partial\varphi_{i,j}(\mathbf{q}_i, \; \omega_i)/\partial\mathbf{q}_i = \int_{v_j} d\mathbf{q}_j \int_{\Omega_j} d\omega_j \partial\varPhi(\mathbf{q}_i, \; \omega_i, \; \mathbf{q}_j, \; \omega_j)/\partial\mathbf{q}_i F_{ij}(\mathbf{q}_i, \; \omega_i, \; \mathbf{q}_j, \; \omega_j)/F_i(\mathbf{q}_i, \; \omega_i), \tag{8}$$

$$\partial\varphi_{i,j}(\mathbf{q}_i, \; \omega_i)/\partial\omega_i = \int_{v_j} d\mathbf{q}_j \int_{\Omega_j} d\omega_j \partial\varPhi(\mathbf{q}_i, \; \omega_i, \; \mathbf{q}_j, \; \omega_j)/\partial\omega_i F_{ij}(\mathbf{q}_i, \; \omega_i, \; \mathbf{q}_j, \; \omega_j)/F_i(\mathbf{q}_i, \; \omega_i). \tag{9}$$

The quantities (8) and (9) are the mean force and mean torque acting on a molecule in cell i due to the molecule in cell j, where the state of the latter is averaged. Similar expressions can be obtained for the potential using the sum in (7), but here the three-particle distribution function is involved, and so (1) and (2) are not closed equations. In order to close this system of equations, we decompose the mean force potentials into irreducible parts [13]. In the case considered here we have

$$\varphi_{ij,l}(\mathbf{q}_i, \; \omega_i, \; \mathbf{q}_j, \; \omega_j) = \varphi_{i,l}(\mathbf{q}_i, \; \omega_i) + \varphi_{j,l}(\mathbf{q}_j, \; \omega_j) + \xi_{ij,l}(\mathbf{q}_i, \; \omega_i, \; \mathbf{q}_j, \; \omega_j). \tag{10}$$

If the irreducible part of the potential is set equal to zero:

$$\xi_{ij,l}(\mathbf{q}_i, \; \omega_i, \; \mathbf{q}_j, \; \omega_j) = 0, \tag{11}$$

which corresponds to neglecting three-particle and higher-order correlations, the expression for the binary function takes the form

$$F_{ij}(\mathbf{q}_i, \; \omega_i, \; \mathbf{q}_j, \; \omega_j) = \exp\{\beta [\varphi_{i,j}(\mathbf{q}_i, \; \omega_i) + \varphi_{j,i}(\mathbf{q}_j, \; \omega_j) - \varPhi(\mathbf{q}_i, \; \omega_i, \; \mathbf{q}_j, \; \omega_j)]\} F_i(\mathbf{q}_i, \; \omega_i) F_j(\mathbf{q}_j, \; \omega_j). \tag{12}$$

The exponential factor in this expression reflects the correlation between molecules and distinguishes the approach used here from the mean field approximation. The approximation (11) corresponds to the quasichemical approximation in the theory of solutions [14].
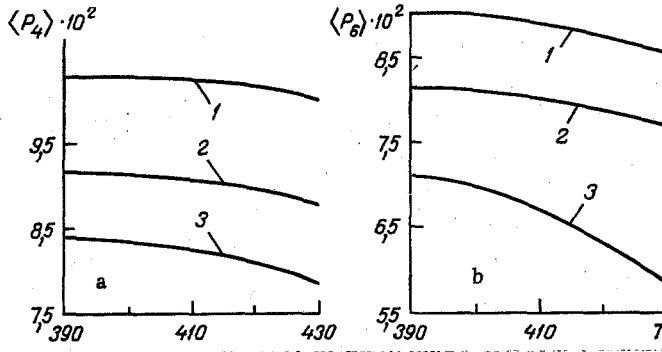
Fig. 2. Temperature dependence of the correlation functions $\langle P_4 \rangle$ (a) and $\langle P_6 \rangle$ (b) for different values of the ellipticity parameter: $\chi = 2.0$ (1), 2.5 (2), 3.0 (3).

Substitution of (12) into (2) leads to a closed system of nonlinear integral equations for the mean force potentials:

$$\exp\{-\beta\varphi_{i,j}(\mathbf{q}_i,\ \omega_i)\} = \int_{v_j} d\mathbf{q}_j \int_{\Omega_j} d\omega_j \exp\{\beta\,[\varphi_{j,i}(\mathbf{q}_j,\ \omega_j) - \Phi(\mathbf{q}_i,\ \omega_i,\ \mathbf{q}_j,\ \omega_j)]\}\, F_j(\mathbf{q}_j,\ \omega_j). \tag{13}$$

Knowing the solution of this system, one can compute the microscopic characteristics of nematics (expressed in terms of the one-particle and two-particle distribution functions) and also the macroscopic characteristics, which can be expressed in terms of the free energy of the system. The free energy per molecule is given by

$$f = -\beta^{-1}\ln Q, \tag{14}$$

where Q is defined by (5). The remaining macroscopic characteristics can be calculated from (14) in the usual way.

Model of the Molecular Interactions and Solution of the Nonlinear Integral Equations. The kernel of the integral equation (13) is determined by the molecular interaction potential. We chose the interaction potential of two molecules in the form [15]

$$\Phi(\mathbf{e}_i,\ \mathbf{e}_j,\ r_{ij}) = \frac{4\varepsilon_0\varepsilon(\mathbf{e}_i,\ \mathbf{e}_j)}{\sigma^2(\mathbf{e}_i,\ \mathbf{e}_j,\ \mathbf{e}_{ij})}\left\{\left[\frac{\sigma_0\sigma(\mathbf{e}_i,\ \mathbf{e}_j,\ \mathbf{e}_{ij})}{r_{ij}}\right]^{12} - \left[\frac{\sigma_0\sigma(\mathbf{e}_i,\ \mathbf{e}_j,\ \mathbf{e}_{ij})}{r_{ij}}\right]^6\right\}, \tag{15}$$

which is constructed from the Lifshits–MacLaughlin theory. Here the following orientation dependence is used for ε and σ [16]:

$$\varepsilon(\mathbf{e}_i,\ \mathbf{e}_j) = [1 - \chi^2(\mathbf{e}_i\cdot\mathbf{e}_j)]^{-1/2},$$

$$\sigma(\mathbf{e}_i,\ \mathbf{e}_j,\ \mathbf{e}_{ij}) = \{1 - \chi/2\,[(\mathbf{e}_i\cdot\mathbf{e}_{ij} + \mathbf{e}_j\cdot\mathbf{e}_{ij})^2/(1 + \chi\mathbf{e}_i\cdot\mathbf{e}_j) + (\mathbf{e}_i\cdot\mathbf{e}_{ij} - \mathbf{e}_j\cdot\mathbf{e}_{ij})^2/(1 - \chi\mathbf{e}_i\cdot\mathbf{e}_j)]\}^{-1/2},$$

$$\chi = (\sigma_\parallel^2 - \sigma_\perp^2)/(\sigma_\parallel^2 + \sigma_\perp^2). \tag{16}$$

Here $\sigma_\parallel$, $\sigma_\perp$ are the axes of the ellipsoid; $r_{ij} = \mathbf{q}_j - \mathbf{q}_i$; $\mathbf{e}_{ij} = r_{ij}/r_{ij}$; $\mathbf{e}_i$, $\mathbf{e}_j$ are unit vectors along the long axes of the two molecules; ε_0 is the energy parameter of the potential; χ is the ellipticity parameter, which characterizes the elongation, or anisotropy, of the molecule.

It is convenient to rewrite (13) in the form

$$\psi_{i,j}(\mathbf{Q}_i) = \left\{\int_{V_j} d\mathbf{Q}_j K(\mathbf{Q}_i,\ \mathbf{Q}_j)\,\psi_j(\mathbf{Q}_j)/\psi_{j,i}(\mathbf{Q}_j)\right\}\Big/\int_{V_j} d\mathbf{Q}_j\psi_j(\mathbf{Q}_j), \tag{17}$$

where $\psi_{i,j}(\mathbf{Q}_i) \equiv \exp\{-\beta\varphi_{i,j}(\mathbf{Q}_i)\}$; $\psi_j(\mathbf{Q}_j) \equiv \exp\{-\beta\varphi_j(\mathbf{Q}_j)\}$; $K(\mathbf{Q}_i,\ \mathbf{Q}_j) \equiv \exp\{-\beta\Phi(\mathbf{Q}_i,\ \mathbf{Q}_j)\}$; $\mathbf{Q}_j$ is a vector in the five-dimensional space $V_j = v_j \oplus \Omega_j$.

Nonlinear equations of this type have been studied by A. S. Kronrod (see [17]), but in the one-dimensional case and with $\psi_j(\mathbf{Q}_j) = 1$. He proved the existence and uniqueness of the solution when certain requirements on the kernel of the equation are satisfied. In our case these requirements are satisfied, and the solution can be found using successive approximations calculated from the formula
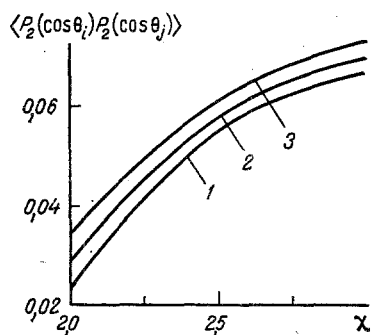
Fig. 3   Fig. 4

Fig. 3. Dependence of the orientational correlation function of two molecules on the ellipticity parameter for the same values of θ as in Fig. 1b.
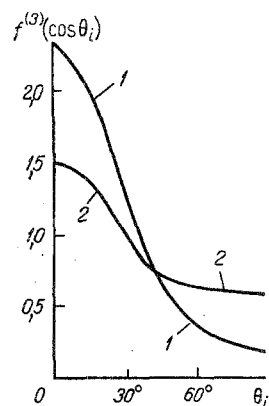
Fig. 4. "Truncated" orientational distribution function for $\theta = 0.75$ (1) and $\theta = 0.7885$ (2).

$$\psi_{n+1}(x) = \left\{ \psi_n(x) \int_v dy K \left(|x - y| \right)/\psi_n(y) \right\}^{1/2}, \tag{18}$$

and the solution does not depend on the initial approximation.

One would hope that this approach could also be applied (with appropriate modifications) to Eq. (17). The basic difficulty in solving the equation is that the algorithm (18) requires the successive evaluation of five-dimensional integrals. The implementation of this procedure requires excessive execution time, when the procedure is required to converge to within a given error (see [18], for example). Statistical methods of the Monte Carlo type cannot be applied because the equation is nonlinear. We used a very simple formula to evaluate the multidimensional integrals:

$$\int_0^1 dx_1 \ldots \int_0^1 dx_n f(x_1, \ldots, x_n) \cong \frac{1}{N} \sum_{\alpha=0}^{N-1} f(Q_\alpha), \tag{19}$$

in which the points Q_α were taken to be the points of a uniformly distributed LP_τ sequence [19], where this sequence is fixed, unlike the quasi-random sequences generated in the Monte Carlo method. This means that we can also use an LP_τ sequence in implementing an algorithm of the type (18) for Eq. (17). The error in the calculation of a multidimensional integral with this approach is $R = O(N^{-1}\ln^n N)$, where n is the dimensionality of the integral. Cubic cells were chosen, where the cells form a simple cubic structure with six nearest neighbors, which were also taken into account in the calculations. This restriction was dictated by the computer available for the study. The total five-dimensional volume of the variables was reduced to a five-dimensional unit cube. The following symmetry property was used in the calculations: the boundary between any two cells is a plane of symmetry for the potentials. Also the total potential does not depend on the number of the cell in an infinite system; this is equivalent to the introduction of long-range order in the system.

The implementation of the algorithm (18) for Eq. (17) was done as follows. The initial approximation was chosen to be $\psi_{j,i}^0(Q_j) = \psi_j^0(Q_j) = 1$. Then the integral on the right-hand side of (17) was calculated according to (23) with the help of a LP_τ sequence. This procedure was repeated for all six neighbors of the particle in cell i. The coordinate Q_i in the kernel $K(Q_i, Q_j)$ was chosen such that $\psi_{i,j}^{(1)}(Q_i)$ would be calculated at the points forming the same stationary LP_τ sequences as that used in the evaluation of the integrals with the initial approximation $\psi_{j,i}^{(0)}(Q_j)$. Then $\psi_i(Q_i)$ was calculated by simple multiplication of $\psi_{i,j}(Q_j)$. The procedure was then iterated until a given accuracy was achieved, where the translational invariance of the total potential was taken into account. The resulting solution then determines the one-particle and two-particle functions (3) and (12), and

also the free energy (14). Knowing the distribution functions, we can calculate the pressure

$$P = \beta/(3v) - 1/(6v) \int_{V_i} d\mathbf{Q}_i \int_{V_j} d\mathbf{Q}_j\,(\mathbf{q}_j - \mathbf{q}_i) \cdot \nabla \Phi(\mathbf{Q}_i, \mathbf{Q}_j)\,F_{ij}(\mathbf{Q}_i, \mathbf{Q}_j), \qquad (20)$$

and also the quantities determining the angular correlations between molecules:

$$\langle P_2(\cos\theta_i) \rangle = (2\langle \cos^2\theta_i \rangle - 1)/2, \qquad (21)$$

$$\langle P_4(\cos\theta_i) \rangle = (35\langle \cos^4\theta_i \rangle - 30\langle \cos^2\theta_i \rangle + 3)/8, \qquad (22)$$

$$\langle P_6(\cos\theta_i) \rangle = (232\langle \cos^6\theta_i \rangle - 315\langle \cos\theta_i \rangle + 105\langle \cos^2\theta_i \rangle - 5)/16, \qquad (23)$$

$$\langle P_2(\cos\theta_i) P_2(\cos\theta_j) \rangle = [9\langle \cos^2\theta_i \cos^2\theta_j \rangle - 3\langle \cos^2\theta_i \rangle - 3\langle \cos^2\theta_j \rangle + 1]/4. \qquad (24)$$

The first three correlation functions are the coefficients of an expansion of the orientational distribution function in a series of Legendre polynomials

$$f(\cos\theta_i) = \sum_{l=0}^{\infty} \frac{2l+1}{2}\,\langle P_l(\cos\theta_i) \rangle P_l(\cos\theta_i), \qquad (25)$$

where $P_l(\cos\theta_i)$ is the Legendre polynomial of order l. These coefficients are used to calculate the "truncated" distribution function $f^{(M)}(\cos\theta_i)$, where M is the number of terms retained in the series.

Since the only input information to the theory is the molecular interaction potential (15), the choice of the parameters of this potential strongly affect the results. This feature of the theory allows one to follow the effect of the potential parameters on the structural and thermodynamic characteristics of nematic liquid crystals.

Explicit calculations were performed for the nematic PAA with the values $\sigma_0 = 5.01$ Å, $\varepsilon/k_B = 520$ K (k_B is the Boltzmann constant) and are shown in Figs. 1 through 4. The ellipticity parameter was varied between 2 and 3 in the calculations.

The calculation of the order parameter (Fig. 1) shows that it decreases with increasing temperature; this agrees with the experimental results [20]. However, the order parameter increases with increasing ellipticity parameter. The correlation functions (21) and (23) decrease as the order of the polynomial increases (Fig. 2) and the temperature dependence of these parameters is roughly the same as that for the order parameter. The values of these parameters decrease as the ellipticity parameter increases. The correlation of the angular positions of two nearest-neighbor molecules increases slightly with increasing temperature, and strongly increases with increasing ellipticity parameter (Fig. 3). The ellipticity parameter has an insignificant effect on the truncated distribution function; with increasing temperature $f(\cos\theta_i)$ tends to smooth out, and this reflects orientational disorder in the nematic liquid crystal (Fig. 4).

Both the orders of magnitude of the quantities and the nature of the dependence of the results are consistent with the known results obtained using other approaches [1]. The method here can be used to calculate a wide spectrum of macroscopic characteristics of nematics, such as the dielectric constant [21], and correlation functions of different orders [22], including correlations between the angular and spatial variables.

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THERMAL ANALYSIS APPLIED TO CHLOROMYCETIN PRODUCTS

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Studies have been made on the physicochemical processes in heat treating chloromycetin semifinished products, and optimum conditions have been defined for heat treatment and drying.

Thermal analysis is increasingly applied to the physical and chemical processes in drying materials [1] because modern instruments provide improved resolving power and new approaches have been devised providing for quantitative results in drying kinetics and mechanisms [2].

Particular interest is attached to determining transition temperatures related to water removal and reactions, since this enables one to forecast the best temperatures for heat treatment and drying and to determine thermal effects accompanying the processes, as well as thermophysical characteristics.

We have used an MOM derivative recorder made in Hungary [3] to examine the physicochemical processes in treating synthetic broad-spectrum antibiotics: chloromycetin and semifinished products from it: threoamin, levoamin, an oxymethyl compound, and dextramin. Figures 1-4 show the recordings. The masses were 400-680 mg, heating temperatures not more than 250°C, heating rates 2.5-10°C/min, sensitivity in TG curve recording 200 mg, DTA and DTG 1/15. Oven atmosphere was air. All the experiments were performed with open ceramic crucibles.

Figure 1a shows that chloromycetin has three effects, peaks at t = 75-110, 140-150, 175°C and above in accordance with the heating rate. The effect at 75-110°C is due to free-water loss. The mass loss in the range 25-110°C lasts for 15 to 40 min, during which up to 30% of the water is lost, which coincides with the initial water content determined by the vapor-pressure method. The subsequent effects characterize the individual features.