Static and Hydrodynamic Properties of Nematic Liquid Crystals*
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Z. Naturforsch. 47a, 565–572 (1992); received January 8, 1992

The static properties of nematic liquid crystals are summarized. The mean field potential emerging from the static distribution function has been used to the hydrodynamic theory. Rotational viscosity coefficients have been investigated. The Parodi relation has been shown to be completely satisfied. Static and hydrodynamic properties have been predicted on the basis of one intermolecular potential.

1. Introduction

Within the framework of the mean field approximation it is possible to derive the description of a number of thermodynamic, static and hydrodynamic properties of nematic liquid crystals on the basis of the same intermolecular potential. As far as we know there is no united realistic microscopic theory which can describe simultaneously static and dynamic properties such as: order parameters, temperature of phase transition, elastic constants and viscosity coefficients. Such theory can be obtained by unification of achievements of Sokalski and Ruijgrok in statics [1, 3] and Osipov and Terentiev in hydrodynamics [2]. It is the purpose of this paper to show some viscosity properties from the point of view of the abovementioned united theory.

The starting point of this theory is the intermolecular potential of two interacting nematic particles. This is described in Chapter 2. The static single particle distribution function and static properties as, for instance, Frank constants are introduced in Chapter 3. Chapter 4 shows the main ideas of Osipov and Terentiev’s approach to hydrodynamics. The unification of statics and hydrodynamic and numerical results of the rotational viscosity coefficients for MBBA are presented in Chapter 5.

2. The Intermolecular Potential

The potential energy of two uniaxial molecules, whose centres are separated by a vector $r$ and whose long axes are parallel to the unit vectors $\mathbf{n}_1$ and $\mathbf{n}_2$ is a function $U(r, \mathbf{A}, \mathbf{n}_1, \mathbf{n}_2)$, where $r$ is the length of $r$ and $\mathbf{A}$ is the unit vector in the direction of $r$. It has a well known general form of the Lennard-Jones type interaction:

$$U = 4\varepsilon \left( \frac{\sigma}{r} \right)^{12} - 2 \left( \frac{\sigma}{r} \right)^6.$$  (2.1)

Ruijgrok [3] came up with a modified form of $\sigma$, which is dependent on the orientation of molecules:

$$\sigma = \sigma_0 + \sigma_1 (\mathbf{A} \cdot \mathbf{n}_1)^2 + \sigma_2 (\mathbf{n}_1 \cdot \mathbf{n}_2)^2.$$  (2.2)

where $\sigma_0$, $\sigma_1$, $\sigma_2$ are fixed parameters connected with the shape of molecules. The parameter $\varepsilon$ is the minimum of the interaction energy multiplied by a factor which depends only on $m$ and $n$. $\varepsilon$, $\sigma_0$, $\sigma_1$, $\sigma_2$, $m$ and $n$ are the only parameters in the calculations and are determined by a fit to the experimental data for the elastic constants. Two interacting molecules are shown in Figure 1.

The closest approach of two interacting molecules is due to the equipotential surface described by the equation: $U = 0$. This surface depends on the relative orientation of two molecules. If $\theta$ is the angle between $\mathbf{A}$ and the positive $z$-axis, the equation for this surface

Fig. 1. Model of two interacting molecules.
can be written as
\[ r/\sigma_0 = 1 + 2S_1 \cos^2(\theta) - S_2 \]
for \( n_1 \) and \( n_2 \) parallel to the z-axis
\[ (\sigma_1 = S_1 \cdot \sigma_0, \quad \sigma_2 = S_2 \cdot \sigma_0), \]
and as
\[ r/\sigma_0 = 1 + S_1 \]
for \( n_1 \) and \( n_2 \) orthogonal to the z-axis.

In the case of (2.4) the surface is a sphere with a radius proportional to \( 1 + S_1 \). In Fig. 2 we have presented the cross section of these surfaces with the \( x-z \) axis plane for two relative orientations of \( n_1 \) and \( n_2 \) for the parameters convenient for MBBA \((S_1 = 0.55, S_2 = -0.25)\).

The closest approach is in accordance with the shape of the molecules. To find the exact relationship between the equipotential surface and the real molecular structure is a very difficult task, and it is not known up till now.

In Fig. 3 we have shown the different regions into which the \( S_1-S_2 \) parameter plane can be divided. The requirement that two molecules have a positive distance of closest approach imposes the restriction \( S_2 < 1 \). From the stability conditions it is found that in this diagram we have the following phases:

1) no stable solution,
2) antinematic phase,
3) nematic phase,
4) nematic phase (including disclike nematics),
metastable phases P, C. They are described in [1].

The important facts emerging from this diagram phase are:

a) Potentials belonging to the first region describe interactions between molecules which do not form any mesophase with translational symmetry. This means that this part of the parameter space contains only the isotropic liquid to solid phase transition lines. In this respect that theory is much better then the Mayer-Saupe [4], McMillan [5], and Rounis-Rosenblatt [6] theories which predict that an isotropic to mesophase transition is always possible.

b) The theory is very sensitive to the potential parameters. A little change of the parameters, \( S_1, S_2 \) near the boundary lines I–II, I–III does not change the “shape” of molecules, whereas it may change the region of the parameter space. This means that minor changes of electric charge distribution around the molecule determine whether the phase can be mesogenic or not.

c) The theory predicts different types of phases.

All these arguments justify the mean field potential \((U_{\text{min}})\) which emerges from the theory of statics based on the Ruijgrok, Sokalski intermolecular potential.

3. The Single Particle Distribution and Static Properties of Nematics

In the paper [7] Stecki and Kloczkowski, following Onsager, have shown that for a system of elongated molecules the free energy can be given explicitly in the form of a cluster expansion containing the Mayer function \( f_{ij} = \exp(-\beta U_{ij}) - 1 \) and the single-particle distribution function \( g(r, n) \) which is a function of the position and orientation of the molecules. Nor-
malization of this function is given by
\[ \int g(r, n) \, dr \, dn = N = V \cdot d. \] (3.1)

The formula of Stecki and Kloczkowski [7] reads
\[ \beta F = \int g(r, n) \, [\log g(r, n) - 1] \, dr \, dn \]
\[ - \frac{1}{2} \int f_{12} g(r_1, n_1) g(r_2, n_2) \, dr_1 \, dn_1 \, dr_2 \, dn_2, \]
where higher order terms are neglected.

The condition of minimum of free energy leads to an equation of the Hammerstein type:
\[ \log g(r_1, n_1) - \int f_{12} g(r_2, n_2) \, dr_2 \, dn_2 = \text{const}. \] (3.3)

For the undistorted nematic \( g \) is uniform in space and axially symmetric around a fixed direction and will be in general a function of \( \cos \theta \) (where \( \theta \) is the polar angle of \( n \)). By introducing the function \( f(x) = \frac{4\pi}{d} g(x) \), which is normalized as \( \int f(x) \, dx = 1 \), (7) can be written as
\[ \log f(x_1) - d/4\pi \int f(x) \, dx \cdot [\exp(-\beta U_{12}) - 1] \, dr_2 \, dn_2 = \text{const}, \]
where \( U_{12} \) is given by (2.1). The radial integration over \( dr_2 = r^2 \, dr \, dA \) can be performed, giving
\[ \frac{1}{\lambda} \int [\exp(-\beta U_{12}) - 1] r^2 \, dr = 1/3 \sigma^2 B_2^* (T^*). \] (3.5)

The reduced second virial coefficient \( B_2^* (T^*) \) is a function of the reduced temperature \( T^* = kT/e \). Using the abbreviation
\[ \lambda = -\pi/6 \sigma_0^2 B_2^* (T^*) \, d, \] (3.6)
(3.4) becomes
\[ \log f(x) - \lambda \int K(x, y) \, f(y) \, dy = \text{const} \] (3.7)
with the symmetric kernel (\( y = \cos \theta \))
\[ K(x, y) = 1/\pi^2 \int [1 + S_1(n_1 \cdot A)^2 + S_1(n_2 \cdot A)^2 - S_2(n_1 \cdot n_2)^2]^3 \, d\phi_2 \, dA. \] (3.8)

The kernel can be represented by a polynomial of sixth order in \( x \) and \( y \) of the form
\[ K(x, y) = \sum_{i,j=0}^3 \alpha_{ij} x^{2i} y^{2j}. \] (3.9)

The symmetric coefficients \( \alpha_{ij} \) are again polynomials in \( S_1 \) and \( S_2 \) of order not higher than three (they are listed in [3]).

The type of the kernel shows that \( \chi(x) = \log f(x) \) must have the form
\[ \chi(x) = c_0 + c_1 x^2 + c_2 x^4 + c_3 x^6. \] (3.10)

Writing
\[ K(x, y) = \sum_{i=0}^3 x^{2i} G_i(y) \] (3.11)
with
\[ G_i(y) = \sum_{j=0}^3 \alpha_{ij} y^{2j}, \] (3.12)
the equation for the coefficients \( c_i \) becomes
\[ c_i = \lambda \int G_i(y) \exp(c_0 + c_1 y^2 + c_2 y^4 + c_3 y^6) \, dy, \] (3.13)
\[ (i = 1, 2, 3). \]

These together with the normalization (3.1), which now reads \( 1 = \int f(y) \, dy \), determine the distribution function completely. It should be remarked that the (uninteresting) uniform distribution \( f(x) = 1 \) is always a solution of (3.7) for any value of \( \lambda \). There is a critical value of \( \lambda_0 \) to be denoted by \( \lambda_0 \), at which a nontrivial solution makes its appearance. Since the order parameter
\[ \langle P_2 \rangle = \frac{1}{\lambda} \int P_2(x) \, f(x) \, dx \] (3.14)
shows a discontinuity at this point, the temperature \( T_c \) corresponding to this \( \lambda_0 \) according to (3.6) will be identified with the experimental value of the critical temperature. The critical value of \( \lambda_0 \) corresponds to the crossing point of the free energies for the isotropic and nematic solutions.

In Fig. 4 the distribution function for MBBA according to theory and experiment is compared.

Figure 5 shows the order parameters \( P_2 \) and \( P_4 \).

Poniewierski and Stecki [13] have shown that in the mean field approximation the elastic constants for splay, bend and twist are given by the following integrals over orientations and the relative distance \( u = r_1 - r_2 \) of two molecules:
\[ K_1 = kT/2 \int u_1^2 c_0(u, n_1, n_2) g_0(\cos \theta_1) g_0(\cos \theta_2) n_{1x} n_{2x} \, dn_1 \, dn_2 \, du, \] (3.15)
\[ K_2 = kT/2 \int u_1^2 c_0(u, n_1, n_2) g_0(\cos \theta_1) g_0(\cos \theta_2) n_{1y} n_{2y} \, dn_1 \, dn_2 \, du, \] (3.16)
\[ K_3 = kT/2 \int u_1^2 c_0(u, n_1, n_2) g_0(\cos \theta_1) g_0(\cos \theta_2) n_{1z} n_{2z} \, dn_1 \, dn_2 \, du. \] (3.17)
Here \( \rho'_0 = d\rho_0(x)/dx \) is the derivative of the single-particle distribution function for the undistorted system as calculated above. The direct correlation function

\[
c_0(u, n_1, n_2) = \frac{\delta^2 \beta F}{\delta \rho(n_1) \delta \rho(n_2)} \tag{3.18}
\]

is in the present approximation, where higher order terms in (3.2) are neglected, given by \( c_0(u, n_1, n_2) = \exp(-\beta U_{12}) - 1 \).

The Frank constants can be calculated using these expressions. The numerical results and the comparison with experimental data are shown in Figure 6.

Since the single-particle distribution function should have the form of \( \exp(-\beta U_{\text{min}}) \) we can regard our \( \chi(x) = c_0 + c_1 x^2 + c_2 x^4 + c_3 x^6 \) as the mean field potential multiplied by the factor \(-kT\),

\[
\chi = (-kT \cdot U_{\text{min}}), \tag{3.19}
\]

which is crucial in the kinetic theory and hydrodynamic properties.

4. Hydrodynamics

The hydrodynamic theory of nematic liquid crystals formulated by Leslie and Ericksen is determined by the corresponding viscous stress tensor

\[
\sigma_{\alpha\beta} = \alpha_1 n_\alpha n_\beta + \alpha_2 n_\alpha A_{\mu\beta} + \alpha_3 n_\alpha n_\beta n_\gamma A_{\mu\gamma} + \alpha_4 A_{\alpha\beta} + \alpha_5 n_\alpha n_\beta N_\mu + \alpha_6 n_\alpha n_\beta n_\gamma n_\delta A_{\mu\gamma\delta}, \tag{4.1}
\]

where \( A_{\alpha\beta} = 1/2(\hat{\alpha}_\alpha v_\beta + \hat{\alpha}_\beta v_\alpha) \) is the symmetrical part of the flow velocity gradients. The possible rotations of the system are reflected by the vector \( N_\alpha = \hat{n}_\alpha - (\omega \times n)_\alpha \), where \( \omega = 1/2 \text{ rot } v \) is the flow rotation angular velocity.

The viscosity constants \( \alpha_1 - \alpha_6 \), the so called Leslie coefficients, are typical for the nematic phase. In the isotropic phase all of them vanish except \( \alpha_4 \), which becomes the isotropic shear viscosity coefficient. The Leslie coefficients must satisfy the general Parodi relation

\[
\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5. \tag{4.2}
\]

This means that there are five independent coefficients. Three of them are connected with the symmetrical part of the viscous stress tensor and the other two with the antisymmetrical part

\[
\sigma_{\alpha\beta}^{\text{sym}} = \frac{\gamma_1}{2} (n_\beta N_\alpha - n_\alpha N_\beta) + \frac{\gamma_2}{2} (n_\beta n_\gamma A_{\mu\gamma} - n_\alpha n_\beta A_{\mu\beta}),
\]

\[
\gamma_1 = \alpha_3 - \alpha_2, \quad \gamma_2 = \alpha_6 - \alpha_5. \tag{4.3}
\]
The coefficients $\gamma$ determine the viscous volume torque on the molecules. The coefficient $\gamma_1$ is characteristic for the viscous torque associated with the angular velocity of the director while $\gamma_2$ gives the contribution to this torque due to the shear velocity in the liquid. $\gamma_1$ is a very important parameter in electro-optic applications employing an LC because the response time of the LC device is proportional to $\gamma_1$, and therefore this coefficient is of special interest. The $\gamma_i$'s are closely related to the flow-alignment angle $\theta$ defined as the angle between the direction of flow and the director under stationary shear flow

$$\cos 2\theta = -\gamma_1/\gamma_2.$$  

(4.4)

Several theories have been developed in an attempt to account for the origin of the viscosity of an LC. They are summarized in [15]. However these theoretical results are not yet completely satisfactory. Some models fit certain LC's but fail to fit others. None of them is connected with the theory which predicts the static properties of nematics. Recently Ospov and Terentiev (OT) developed a microscopic theory for describing the origins of LC viscosities. However, since they have not been able to use the proper mean field potential, their results are not completely satisfactory either. In this chapter the main ideas of the OT theory are introduced. The major purpose is the calculation of the nonequilibrium distribution function which characterizes the statistical properties of the flowing nematic. Then the viscosity coefficients of an LC can be obtained by averaging the microscopic stress tensor. The expression for the microscopic stress tensor for a liquid composed of anisotropic molecules has the following form:

$$\sigma_{xy}^{sym} = \frac{1}{2} \left[ a_x \frac{\partial U_{min}}{\partial a_y} - a_y \frac{\partial U_{min}}{\partial a_x} \right],$$

$$\sigma_{xy}^{sym} = \frac{p^2-1}{p^2+1} \left[ 3kT(a_xa_y - \frac{1}{3}\delta_{xy}) + \frac{1}{2} \left[ a_x \frac{\partial U_{min}}{\partial a_y} + a_y \frac{\partial U_{min}}{\partial a_x} \right] \right].$$  

(4.5)

This formula is derived using the method introduced in paper of Kuzuu and Doi [16]. The angle dependence of this microscopic stress tensor is described by the orientation of the long molecular axis with respect to the direction $n$ which is determined by the polar ($\theta$) and azimuthal ($\phi$) angles,

$$a = n \cos \theta + e \sin \theta, \quad e_x = \cos \phi, \quad e_y = \sin \phi, \quad e_z = 0.$$  

(4.6)

It should be noted that the equilibrium one particle distribution function depends only on $\theta$. As far as the flowing nematic in the molecular field approximation is concerned the nonequilibrium single particle distribution function must depend on both angles $f(\theta, \phi)$. In the case of small velocity gradients this function can be written in the form $f = f_0(1 + h)$, where $f_0$ is the local equilibrium distribution function and the small correction $h$ is proportional to the velocity gradients.

The general expression for $h$ should have the form

$$h = g_0 n_x n_\beta A_{x\beta} + g_x n_x e_\beta A_{x\beta} + g_\beta n_\beta A_{x\beta}$$

(4.7)

The macroscopic stress tensor can be written as an average of the microscopic form:

$$\sigma_{xy} = \int f_0 h \sigma_{xy} da.$$  

(4.8)

Comparison of this form of the stress tensor with the form proposed by Leslie and Ericksen yields the corresponding Leslie coefficients provided the functions $g$'s in the correction $h$ are known. The stationary correction $h$ to the equilibrium distribution function $f_0$ can be calculated with the help of the appropriate kinetic theory. With the assumption that the microscopic molecular motion in an LC can be considered as a rotational Brownian motion in the mean field potential the following kinetic equation determines the nonequilibrium distribution function:

$$\dot{f} + e \dot{\epsilon}_k (f \Omega_k) = e^2 \dot{\epsilon}_k (\hat{\epsilon}_k f - I_k/kT f),$$  

(4.9)
where the differential operator $\partial_k = e_{kij} a_i \partial/\partial a_j$ describes the infinitesimal rotation of the long molecular axis $a$, and $I_k = -\partial_k U_{\text{min}}(a \cdot n)$ is the moment of the force acting on the molecule in the mean field. The average velocity has the form

$$\Omega = \frac{p^2-1}{p^2+1} a \times (A \cdot a) - a \times (g \cdot a)$$  \hspace{1cm} (4.10)

and $\varepsilon$, which is the ratio of two characteristic relaxation times of the system, is a small parameter of the theory.

Using this theory, the expressions for $\gamma$'s will have the form

$$\gamma_1 = \text{const} \int_0^\theta \partial U_{\text{min}}/\partial \theta \varrho_a \, d(\cos \theta), \hspace{1cm} (4.11a)$$

$$\gamma_2 = \text{const} \int_0^\theta \partial U_{\text{min}}/\partial \theta \varrho_s \, d(\cos \theta), \hspace{1cm} (4.11b)$$

where the functions $\varrho_a$ and $\varrho_s$ can be obtained from the kinetic equation in the form

$$\varrho_a (\theta) = C \int_0^\theta e^{-x/x} \sin x \int_0^x e^{x'/(x')} \sin x' \, d(\cos \theta), \hspace{1cm} (4.12a)$$

$$\varrho_s (\theta) = C \int_0^\theta e^{-x/x} \sin x \int_0^x e^{x'/(x')} \sin x' \, d(\cos \theta), \hspace{1cm} (4.12b)$$

where $C$ is a constant.

Results of applying the mean field potential from statics to these expressions are presented in the next chapter.

5. Rotational Viscosity for MBBA

By application of the mean field potential $U_{\text{min}}$ (3.19) for MBBA to (4.12a, 4.12b) and then (4.11a, 4.11b) we have obtained the rotational viscosity coefficients $\gamma_1$ and $\gamma_2$ characteristic for MBBA. The obtained temperature dependence and the experimental data from [17], which are recommended as model data, are shown in Figure 7. The agreement theory and experiment is very good. In Fig. 8 the temperature dependence of the extinction angle $\chi$ is presented (cf. 4.4). The dashed line presents results of Osipov and Terentiev theory from paper [18]. The intermolecular potential they have used leads to the best agreement with experiment values of the extinction angle about 15%. Moreover it is not checked if this potential really describes a mesophase state and gives a nematic solution. In our case we are completely sure that our potential describes a nematic. Moreover we can predict all static properties for it as was summarized above. The ratio $\rho = \text{length}/\text{width}$, which is obtained
the expression for $x_2 + x_3$ in the following form
\[
x_2 + x_3 = \text{const } kT \int f_0 [3 \sin \theta \cos \theta + 1/2 \partial U_{\text{min}}/\partial \cos \theta \cos 2\theta] \rho_0 \, d(\cos \theta).
\]

On comparing numerical values for $x_2 + x_3$ with $\gamma_2$ we have obtained almost the same curve, which means that the Parodi relation is fulfilled exactly. This Parodi relation is shown in Figure 9. All these calculations have been done under the assumption that the small parameter $\epsilon$ in the kinetic equation has the form $\epsilon = \epsilon_0 kT$, where $\epsilon_0$ is treated as a fitting parameter. $\epsilon_0$ is the same for all calculations. It is found to be $\epsilon_0 = 1690 \text{ J}$. Only then we obtain such an agreement with experimental data as shown in the figures. The origin and physical meaning of $\epsilon$ is not discussed here. It should be noted that the main dependence on microscopic molecular parameters appears indirectly in the distribution function $f_0$ and in the mean field potential $U_{\text{min}}$, not in the structure of small parameter $\epsilon$.

6. Conclusion

On the basis of the same intermolecular potential, static and hydrodynamic theories are successful in the following areas

a) Static theory [1] predicts properly such properties as: order parameters, distribution function, temperature of the phase transition, elastic constants and equipotential surfaces for molecules in different nematics including disclike ones. Moreover it predicts new types of nematic mesophases. Within the $S_1 - S_2$ parameter space there are areas where only the transition isotropic-solid state is possible, contrary to other theories which predict that isotropic-mesophase transitions are always possible.

b) Rotational viscosity coefficients for MBBA calculated with the hydrodynamic theory and based on the mean field potential emerging from the statics are in a very good agreement with experimental results. The disagreement between theory and experiment for the values of the extinction angle, which is the most sensitive for the accuracy, is about 3%.

The parameter $p = \text{length}/\text{width}$ is found to be about 4, while it is supposed to be 5. From results of
other theories it is predicted to be about 2, however there is no experimental evidence about that.

The intermolecular potential which was used to derive the mean field potential was formed to lead to nematic solutions, while in the case of other theories as for instance [2] we can not be sure if the potential is a real nematic potential.

The Parodi relation in our case is fulfilled exactly. There is a consistent connection between statics and hydrodynamics through the mean field potential, and as a matter of fact the same intermolecular parameters $S_1$ and $S_2$ determine the static and hydrodynamic properties of nematics.