Vol. A56 (1979) *ACTA PHYSICA POLONICA* No 6

ORIENTATIONAL ASPECTS OF THE DISCRETE STATISTICAL MODEL OF NEMATIC PHASE*

BY K. Z. OGORODNIK

Institute of Organic Semiproducts and Dyes, Moscow**

(Received February 28, 1978; final version received May 8, 1979)

The relations that enable one to find the order parameters $\bar{P}_n$ of the angle distribution of the long molecule axes $\vec{a}$, when the values $\bar{P}_n$ for the vectors $\vec{b}$ describing the response of the medium to external influences are known, have been derived. A particular case of the mutual connection between $\vec{a}$ and $\vec{b}$, which corresponds to the discrete statistical model of nematics with a short-range order has been used to explain the differences between the values of $\bar{P}_2$ and $\bar{P}_4$ measured by the EPR and the Raman methods, and the ones predicted by the theory.

The ability to form spontaneously the regions (domains) with some types of order is the principal property of the liquid crystalline (LC) medium. The other properties having a practical significance result from the above one. In the case of a nematic (N) phase the ordered region can be ascribed a direction characterized by vector $\vec{n}$ (called a director). The angle distribution of long molecule axes has a cylindric symmetry. It belongs to the point group $D_{\infty h}$ and is characterized by the element of symmetry C_∞ and σ_h. It is convenent to describe the above distribution by the function $f(\cos\theta)$ of the angle $\theta = \widehat{\vec{a}\vec{n}}$, so that $\int_0^1 f(\cos\theta)d\cos\theta = 1$, and $f(\cos\theta)\sin\theta d\theta$ is equal to the probability of finding the molecule oriented within a cone $[\theta, \theta+d\theta]$.

The microscopic theory of the LC state is expected to explain the nature of the forces providing the order, their connections with the structure of the molecules, and the mechanism determining the temperature interval in which the given type of mesophase exists. Such a theory does not exist yet. The theories explaining the particular properties of a mesophase assume its existence a priori. The theory of Maier and Saupe (MS) [1, 2] is

---

* Presented at the Second Liquid Crystal Conference of Socialist Countries, Sunny Beach, Bulgaria, September 27-30, 1977.

** Address: Nauchno-Issledovatelskii Institut Organicheskikh Poluproduktov i Krasitelei, Moskva, USSR.

most similar to the microscopic theory. This theory agrees with the experiment only qualitatively. Attempts to modify it in order to get a quantitative description of the experiment have failed. As a theory of a mean field, the MS approach ignores the arrangement of the neighbouring molecules, which reflects peculiarities of interactions of real molecules. The idea of a mean field of molecules provides a selfconsistency for the description of the orientational statistics of molecules and, consequently, a prediction of the order-disorder transition. From the moment of discussing the dependence of the orientational potential on the mean molecular volume and, further, the dependence of the latter on temperature, the MS theory ceases to be phenomenologic. The dependence on the density of substance is the veiled form of taking into account the short-range order. One can obtain better agreement with the experiment assuming the simplest model of the short-range order (each four molecules are rigidly connected parallel to each other [2]), but the MS theory with such assumption is no more the theory of mean molecular field. The statistics of molecules is now determined by the statistics of groups of molecules and the distribution inside the group.

The broadening and change in the shape of the Raman spectrum bands, which accompany the fusion of the solid crystalline (SC) form of a substance in the LC state may suggest the existence of polymorphism of the short-range order in the LC melt, i.e. coexistence of several types of short-range order in the mesophase [3]. The Raman spectral studies of SC polymorphs of nematogenics show that for some of them the long axes of molecules form a considerable angle (up to 90°) between one another. The X-ray studies [4] suggest the same. Different SC forms and types of short-range order can be distinguished not only by the geometry of the molecular packing but also by the geometry of the molecules themselves. The conformational changeability and SC polymorphism usually occur together.

The validity of the theory of the orientational statistics can be tested by comparing its predictions with the temperature dependence of the order parameters obtained in the experiment. Under rather general assumptions $f(\cos\theta)$ can be presented as the series [5]

$$f(\cos\theta) = 1+5\bar{P}_2\cdot P_2(\cos\theta)+9\bar{P}_4\cdot P_4(\cos\theta)+\ \ldots, \tag{1}$$

where

$$\bar{P}_n = \int_0^1 P_n(x)\cdot f(x)\cdot dx, \tag{2}$$

and

$$P_2(x) = (3x^2-1)/2, \quad P_4(x) = (35x^4-30x^2+3)/8. \tag{3}$$

Two order parameters can be found from spectral measuring of the luminescence [6, 7], the Raman scattering [8], and EPR [9]. The results obtained by Jen et al. [10, 11] and then by Heger [12] and Miyano [13] by means of the Raman method, and by the luminescence method [7, 14, 15] showed the considerable inconsistency with the theory. On the contrary, the EPR results were in a good agreement with the theory [9, 16] (see Fig. 1).

For the comparison of the order parameters it is convenient to use the coordinate system $\bar{P}_2$, $\bar{P}_4$. The solid curve on Fig. 1 shows the relation between $\bar{P}_2$ and $\bar{P}_4$ in the case of $f(\cos\theta)$ being of the form

$$f(\cos\theta) = \exp\{c_2 P_2(\cos\theta)\}/\int_0^1 \exp\{c_2 P_2(x)\}dx, \tag{4}$$

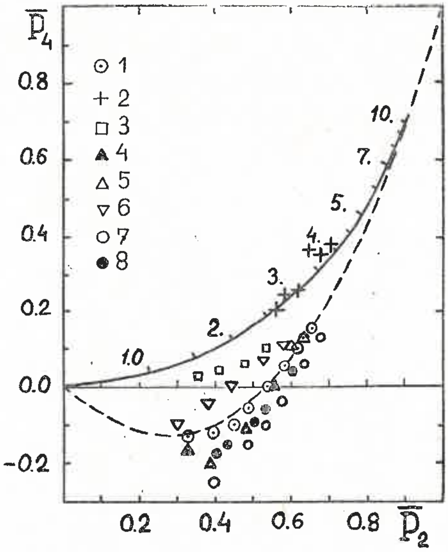

Fig. 1. Experimental values of $\bar{P}_2$ and $\bar{P}_4$: *1, 3, 6* — from references [11–13] respectively, obtained by Raman scattering; *2* — from Ref. [16], obtained by EPR; *4, 5, 7* and *8* — from Ref. [7, 14, 15], obtained by the luminescence method. The solid curve corresponds to the MS theory, the dashed one — to the model of Luckhurst and Yeates

(c_2 is a parameter). This distribution corresponds to the orientational potential of a molecule in the mean field of the surrounding molecules of the form

$$U_1 = -a_2 \cdot P_2(\cos\theta), \tag{5}$$

where a_2 is a positive factor, which does not depend on θ. The set of points $(\bar{P}_2(c_2), \bar{P}_4(c_2))$ represents all possible values of the order parameters corresponding to the MS theory. With the change of temperature, the point $(\bar{P}_2, \bar{P}_4)$ moves along the curve. As there are discrepancies between the above values and the experimental ones [11], a function different from (4) is required in order to provide a correct description of the angular distribution of molecules. The discrepancy mentioned above was discussed in several papers [16–20]. The attempts to find an agreement with the experiment in the frame of the generalised mean field theory led to the following potential

$$U_1(\cos\theta) = u \cdot \bar{P}_2 \cdot P_2(\cos\theta) + u' \cdot \bar{f} \cdot f(\cos\theta),$$

$$f(\cos\theta) = P_2(\cos\theta) - 2P_4(\cos\theta) + P_6(\cos\theta) \tag{6}$$

instead of the one from (5). The distribution corresponding to the potential (6) has a maximum at 52°, but the nematic phase becomes unstable [19]. The other attempts [16–18] do not have a clear physical meaning (the limit cases are understandable, but the intermediate ones do not have any interpretation). It will be shown below that the particular cases of the discrete statistical model have the same mathematical form. The complete picture of the orientational aspects of this model can describe all possible forms of correlations in the arrangement of neighbouring molecules.

Let us consider the following model of a NLC with the short-range order: (*i*) all molecules are divided into groups of anisometric form, the direction of the greatest dimension of a group determining the anisotropy of its properties which are responsible for the interaction between groups; (*ii*) the angle distribution of the molecules in the average group is described by the function $f_{\mathrm{gr}}^{\mathrm{mol}}(\cos\vartheta)$, where $\vartheta = \widehat{\vec{a}\vec{b}}$; (*iii*) the angle distribution of groups of spontaneously ordered regions, here called domains (or of monodomains, sets of domains oriented by external forces) is described by the function $f_{\mathrm{dom}}^{\mathrm{gr}}(\cos\theta')$, where $\theta' = \widehat{\vec{b}\vec{n}}$. The meaning of the introduced angles and vectors is shown on Fig. 2. It can be shown (see Appendix) that for the distribution of the molecules in the domain, $f_{\mathrm{dom}}^{\mathrm{mol}}(\cos\theta)$, the coefficients of the series (1) are determined as

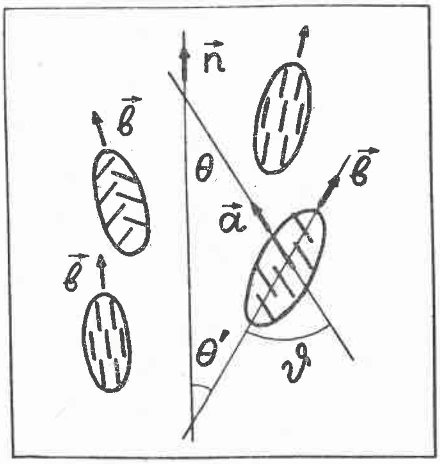

Fig. 2. A sketch of the arrangement of molecules and groups of molecules in a nematic monodomain

$$\bar{P}_n^{\mathrm{MD}} = \bar{P}_n^{\mathrm{MG}}\bar{P}_n^{\mathrm{GD}}. \tag{7}$$

$\bar{P}_n^{\mathrm{MD}}$, $\bar{P}_n^{\mathrm{MG}}$ and $\bar{P}_n^{\mathrm{GD}}$ are defined according to (2) by $f(\cos\theta)$ for molecules in domain, molecules in group, and groups in domain, respectively.

In the particular case, when all molecules in each group form with the axis $\vec{b}$ the same angle β, i.e. when

$$f_{\mathrm{gr}}^{\mathrm{mol}}(\cos\vartheta) = \delta(\cos\vartheta - \cos\beta), \tag{8}$$

where $\delta(a-x)$ is a Dirac δ-function, the formula (7) can be transformed into

$$\bar{P}_n^{\mathrm{MD}} = P_n(\cos\beta)\bar{P}_n^{\mathrm{GD}}. \tag{7a}$$

Let groups inside a domain be distributed according to (4) and, consequently, $\bar{P}_2^{\mathrm{GD}}$ and $\bar{P}_4^{\mathrm{GD}}$ be positive (see Fig. 1). Then the order parameters $\bar{P}_2^{\mathrm{MD}}$, $\bar{P}_4^{\mathrm{MD}}$ become negative, when

$$P_2(\cos\beta) < 0, \quad \beta > \beta_3,$$
$$P_4(\cos\beta) < 0, \quad \beta_4 > \beta > \beta_1,$$

(see Fig. 3).

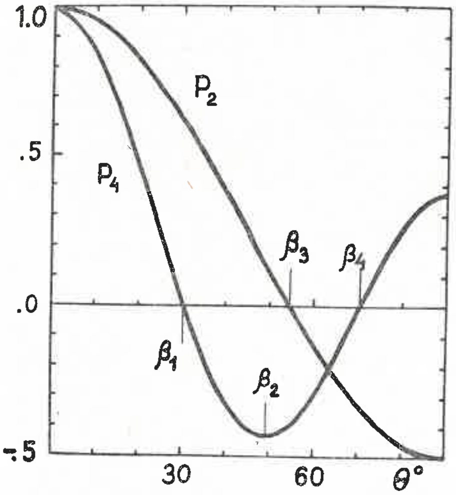

Fig. 3. The angle dependences of the functions $P_2(\cos\theta)$ and $P_4(\cos\theta)$

The relation (7a) can be presented graphically, in the form convenient for practical purposes. The parameters $\bar{P}_2$, $\bar{P}_4$ are chosen as coordinates. As a result, we obtain in Fig. 4 two sets of intersecting curves, denoted as A and B. The lines of the set A join the points on the curve B with the origin. The points $(\bar{P}_2, \bar{P}_4)$ of the curves of the set A correspond to the distribution of molecules in the domain in the case when the groups are distributed according to (4), c_2 is varying from 0 to ∞ and the angle of inclination of molecules in the group is constant. The limit line of this set ($\beta = 0$) corresponds to distributions of MS theory for different values of c_2 (the numbers along this curve). Another set of lines (B) connects points on the curve A with the ordinate axis. The values $\bar{P}_2$, $\bar{P}_4$ on the lines of this series correspond to distribution of molecules in a domain for fixed distribution of groups (c_2 = const.) and for different values of β. The limit line of this set ($c_2 = \infty$) corresponds to the distribution when all groups are parallel to the director and identical (β is the same for all groups). The values of β are given along the limit line.

Every experimental point $(\bar{P}_2, \bar{P}_4)$ determines then the parameters of the group distribution, c_2, and the ones of the distribution of molecules in groups, β, for given model of identical groups and given value of β. We will call this model $\beta 1$. We assume now that we have two types of groups (for $\beta = \beta_1$ and $\beta = \beta_2$) and that the distribution of groups does not depend on β (the model $\beta 2$). Mathematically this model is identical with the case when we have groups of only one type, but inside each group a part of molecules has inclination β_1, and another part has inclination β_2 with respect to the axis $\vec{b}$. For the $\beta 2$ model for each point $(\bar{P}_2, \bar{P}_4)$ situated between the lines $\beta = \beta_1$ and $\beta = \beta_2$ there is a line $c_2 = \text{const}$ such that a straight line connecting the points β_1 and β_2 on this line goes through the given point $(\bar{P}_2, \bar{P}_4)$. The value of c_2 found in this way determines the distribution of groups and the ratio of distances from $(\bar{P}_2, \bar{P}_4)$ to (c_2, β_1) and (c_2, β_2) determines the ratio of number of β_2- and β_1-groups (see Fig. 4). In the general case when there are N types of groups we have, instead of (7a)

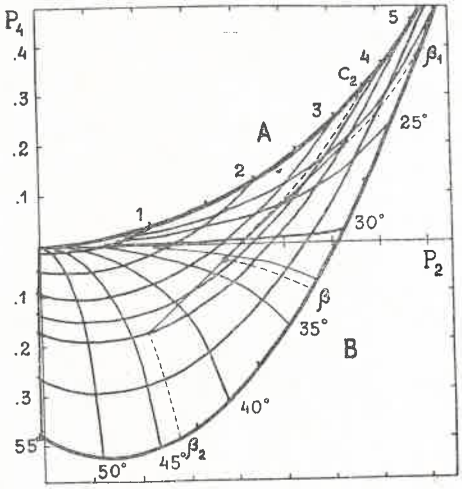

Fig. 4. An example of the application of the relation (7a) to finding graphically the parameters c_2 and β for the model $\beta 1$, and the parameter c_2 and fraction of β_1- and β_2-groups for the model $\beta 2$

$$\bar{P}_n^{\mathrm{MD}} = \bar{P}_n^{\mathrm{GD}} \sum_i k_i P_n(\cos \alpha_i), \qquad i = 1, 2, \ldots, N \tag{7b}$$

where k_i is the fraction of groups of β_i-type, $\sum_i k_i = 1, 0 < \beta_i < \pi/2$. An experimental point $(\bar{P}_2, \bar{P}_4)$ determines now the parameter c_2 characterizing the distribution of groups and the parameter characterizing the distribution of molecules in groups, e.g., the half-width $\Delta\beta_{1/2}$ of $f_{\mathrm{gr}}^{\mathrm{mol}}(\cos \beta)$. We have then many models βN for a given point $(\bar{P}_2, \bar{P}_4)$. We may choose one of them thanks to the information about the number of possible packing, N, and the geometry of packing (values $\beta_1, \beta_2, \ldots \beta_N$). It is natural to consider N to be equal to the number of SC modifications. The problem of finding the fractions k_i is the task for a microscopic theory of NLC state.

Let us assume that a small amount of molecules in the nematics is of such a type that the possibility of packing them jointly with the host molecules of a nematogenics can be excluded. It is then natural to expect that the angle distribution of the guest molecules determined by the EPR or luminescence methods corresponds to the distribution of groups. One can determine the distribution of the host molecules of NLC for the same sample by means of Raman spectroscopy. After having obtained the values of $\bar{P}_2^{\mathrm{MD}}$, $\bar{P}_4^{\mathrm{MD}}$ and $\bar{P}_2^{\mathrm{GD}}$, $\bar{P}_4^{\mathrm{GD}}$ one can find the values of $\bar{P}_2^{\mathrm{MG}}$ and $\bar{P}_4^{\mathrm{MG}}$ with help of (7). The values of $\bar{P}_2^{\mathrm{GD}}$ and $\bar{P}_4^{\mathrm{GD}}$ determine the curve $c_2 = \mathrm{const}$; the distance to this curve from the point $(\bar{P}_2^{\mathrm{MD}}, \bar{P}_4^{\mathrm{MD}})$ limits also the possibilities of choosing the distributions $f_{\mathrm{gr}}^{\mathrm{mol}}(\cos\beta)$ of molecules among the possible kinds of groups.

In conclusion, we compare our explanation of the negative values of the order parameter $\bar{P}_4$ with the one of Luckhurst and Yeates [16, 17]. The latter one consists in following: (*i*) The considerable deviation of the values of $\bar{P}_4$ measured by Raman scattering [11, 12] from the values of $\bar{P}_4$ predicted by the mean molecular field theories results from the uncertainty of the interpretation of light scattering experiments. The authors give as a proof the data for $\bar{P}_4$, provided by the EPR measurements, which are in good agreement with the theory [9, 16] (see also Fig. 1). (*ii*) The experimental values of $\bar{P}_2$ and $\bar{P}_4$ obtained by Jen et al. [10, 11] coincide with the ones from the mean molecular field theory, when the orientational potential $U_1(\theta)$ is assumed to be a rectangular well [17]

$$\begin{aligned} U_1(\theta) &= 0, \qquad \theta < \theta_0, \\ U_1(\theta) &= \infty, \qquad \theta > \theta_0. \end{aligned} \tag{9}$$

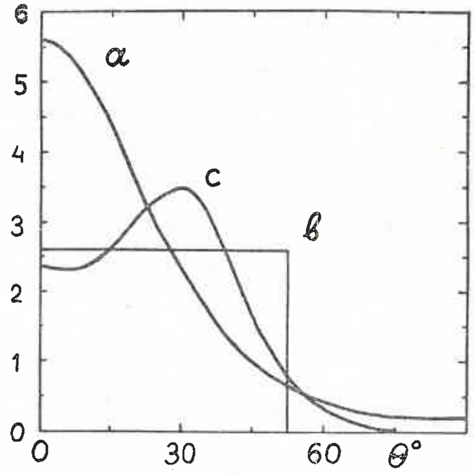

Fig. 5. The probability density of orientations of molecules with respect to the director $\vec{n}$: *a* — the MS model ($c_2 = 2.3$), *b* — the model of Luckhurst and Yeates ($\theta_0 = 52°$), *c* — the discrete statistical model (the groups distributed according to (4): 93% of them correspond to $\beta = 32°$, 7% — to $\beta = 0$; $c_2 = 7.4$)

The relationship of $\bar{P}_4(\theta_0)$ on $\bar{P}_2(\theta_0)$ is shown on Fig. 1 as a dashed line. One assumes here implicitly that $\theta_0 = \theta_0(T)$ is an increasing function of T.

In Fig. 5 the curve *a* represents the function of the probability density of the orientation of molecules forming the angle θ with the director in the case of the MS orientational potential (5) and the curve b represents this function for a potential of the form (9). According to Luckhurst and Yeates [16, 17], the EPR data correspond to the distribution a and the Raman data to b. This contradiction can be explained on the basis of the discrete statistical model of short-range order for a nematics. In fact, by the EPR method one obtains $\bar{P}_2$ and $\bar{P}_4$ of the guest molecules. These molecules are not isomorphic to the molecules of the nematogenics [21] and they are long enough not to be packed inside the crystallizing clusters. In such a case the statistics of the guest molecules correspond to the one for the molecular groups (bodies, clusters), but not for the individual molecules of the nematics.

By means of the Raman scattering method one finds the order parameters of molecules of a nematic medium [8, 11–13]. In this case the distribution of molecules, $f^{\mathrm{mol}}(\theta)$, can differ significantly from the one for the groups, $f^{\mathrm{gr}}(\theta)$, when not all molecules inside the group are aligned parallelly to the direction of the largest dimension of this group. The curve c in Fig. 5 represents the distribution of molecules in the case when the groups are aligned according to the curve a (but with the halfwidth of 29° instead of 53°), while inside groups molecules are inclined at angle 32° to the direction of the largest dimensions of these groups. Both the b and c distributions correspond to the values of $\bar{P}_2$ and $\bar{P}_4$ equal to 0.5 and -0.043, respectively. The distribution b corresponds to the model of nematics in which molecules fluctuate freely in the limits of the angle $\pm\theta_0$ and the distribution c corresponds to the discrete statistical model. Both models explain the possibility of negative values of $\bar{P}_4$: the first one for $\theta_0 > 50°$, the second one for $\beta > \beta_1 = 30.5°$. The second model explains also the peculiarity of the Raman bands broadening which accompanies the melting of the crystal to a nematic phase [3] and is supported by the facts of SC polymorphism of mesogenics [22].

The model of a pure sterical potential (9) in the extremal case is equivalent mathematically to the discrete statistical model in which all the groups are parallel to the director ($\theta' = 0$) and the number of groups characterized by given angle β is equal for each β from segment $(0, \theta_0)$. The points of the dashed curve in Fig. 1 are the centres of gravity of the segments of the curve B from 0° to θ_0. The above model does not cover the values of $\bar{P}_2$ and $\bar{P}_4$ located below the dashed curve in Fig. 1 (as for the point located above this curve, the procedure of formal mixing of the values of the dashed and solid curves in Fig. 1 has been suggested [17]).

APPENDIX

Let the alignment of molecules in the ensemble-averaged group be described by the distribution function $\tilde{f}^{\mathrm{mol}}_{\mathrm{gr}}(\vartheta, \varphi)$, where ϑ and φ are the polar and azimuthal angles between the symmetry axis of the group, $\vec{b}$, and the long molecule axis, $\vec{a}$. The alignment of groups in a nematic monodomain is given by $\tilde{f}^{\mathrm{gr}}_{\mathrm{dom}}(\theta', \phi')$, where θ' and ϕ' are angles between $\vec{b}$ and the director $\vec{n}$. The distribution of molecules in a monodomain $\tilde{f}^{\mathrm{mol}}_{\mathrm{dom}}(\theta, \phi)$, where θ and ϕ are angles between $\vec{a}$ and $\vec{n}$, is defined by the expression

$$\tilde{f}^{\mathrm{mol}}_{\mathrm{dom}}(\theta, \phi) = \iint_S \tilde{f}^{\mathrm{mol}}_{\mathrm{gr}}(\vartheta, \varphi) \cdot \tilde{f}^{\mathrm{gr}}_{\mathrm{dom}}(\theta', \phi') d\sigma, \tag{A1}$$

where S is the surface of the unit sphere, $d\sigma$ is a surface element, $\vartheta = \vartheta(\theta', \theta, \phi-\phi')$, $\varphi = \varphi(\theta', \theta, \phi-\phi')$. Considering $\tilde{f}^{\mathrm{mol}}_{\mathrm{gr}}$ and $\tilde{f}^{\mathrm{gr}}_{\mathrm{dom}}$ as independent on the azimuthal angles (consequently $\tilde{f}^{\mathrm{mol}}_{\mathrm{dom}}$ will also have the cylindrical symmetry), one can use functions dependent only on cosines of the polar angles:

$$2\pi f^{\mathrm{mol}}_{\mathrm{dom}}(\cos\theta) = \iint_S f^{\mathrm{mol}}_{\mathrm{gr}}(\cos\vartheta)\cdot f^{\mathrm{gr}}_{\mathrm{dom}}(\cos\theta')d\sigma. \tag{A2}$$

Let us expand the new functions (without tilde) in the series of Legendre polynomials (Ref. [5], p. 492):

$$f^{\mathrm{mol}}_{\mathrm{dom}}(\cos\theta) = \sum_n \frac{2n+1}{2}\bar{P}^{\mathrm{MD}}_n\cdot P_n(\cos\theta),$$

$$f^{\mathrm{mol}}_{\mathrm{gr}}(\cos\vartheta) = \sum_n \frac{2n+1}{2}\bar{P}^{\mathrm{MG}}_n\cdot P_n(\cos\vartheta),$$

$$f^{\mathrm{gr}}_{\mathrm{dom}}(\cos\theta') = \sum_n \frac{2n+1}{2}\bar{P}^{\mathrm{GD}}_n\cdot P_n(\cos\theta'), \tag{A3}$$

where $\bar{P}_n = \int\limits_{-1}^{1} f(x)\cdot P_n(x)\cdot dx$. Applying the integral formulas from the spherical function theory one obtains

$$\iint_S P_n(\cos\theta')\cdot P_m(\cos\vartheta)d\sigma = \begin{cases} 0, & m \neq n \\ \dfrac{4\pi}{2n+1}P_n(\cos\theta), & m = n. \end{cases} \tag{A4}$$

Substituting (A3) into (A2) and taking into account (A4) one obtains

$$\bar{P}^{\mathrm{MD}}_n = \bar{P}^{\mathrm{MG}}_n\bar{P}^{\mathrm{GD}}_n. \tag{A5}$$

Let us assume the distribution of molecules in groups to be of the form $f^{\mathrm{mol}}_{\mathrm{gr}}(\cos\vartheta) = 1/L\ \delta(\cos\vartheta-\cos\beta)$, then the distribution of the molecules in monodomain is determined by the expression:

$$2\pi\cdot f^{\mathrm{mol}}_{\mathrm{dom}}(\cos\theta) = \frac{1}{L}\iint_S \delta(\cos\vartheta-\cos\beta)f^{\mathrm{gr}}_{\mathrm{dom}}(\cos\theta')d\sigma = \frac{1}{L}\oint_L f^{\mathrm{gr}}_{\mathrm{dom}}(\theta', \phi')dl, \tag{A6}$$

where L is the circle $\cos\theta'\cos\theta-\sin\theta'\sin\theta\cos(\phi-\phi') = \cos\beta$ on the surface of the unit sphere, the radius of the circle is equal to $\sin\beta$, the centre is at the point (θ, ϕ).

The evolution of the distribution (A6) with increasing angle β can be presented by simple example. Let molecules in a group be oriented with equal probability along eight directions symmetric in relation to the axis of the group and inclined to the axis at angle β. In this case instead of (A6) we have

$$f^{\mathrm{mol}}_{\mathrm{dom}}(\cos\theta) = \tfrac{1}{8}\sum_{i=1}^{8} f^{\mathrm{gr}}_{\mathrm{dom}}(x_i), \tag{A7}$$

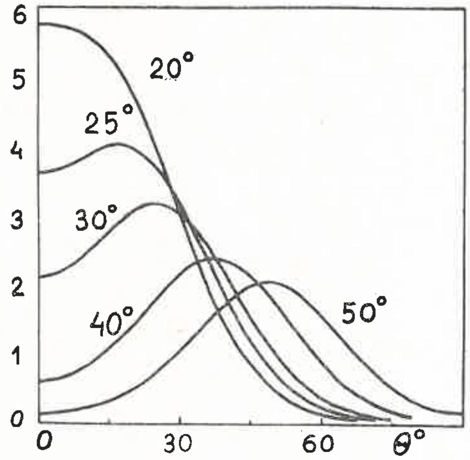

Fig. 6. The angle distributions of molecules with respect to the director, when all the groups are identical and their distribution corresponds to (4) ($c_2 = 5.0$). The numbers near the curves indicate the angles of inclination of molecules to the axis of the group

where $x_1 = \cos(\theta-\beta)$, $x_2 = x_8 = \cos\alpha_0\cos(\theta-\alpha_0)$, $x_5 = \cos(\theta+\beta)$, $x_3 = x_7 = \cos\beta\cos\theta$, $x_4 = x_6 = \cos\alpha_0\cos(\theta+\alpha_1)$, $\alpha_0 = \arcsin(\sin\beta\sin 45°)$, $\alpha_1 = \mathrm{arctg}(\mathrm{tg}\,\beta\cos 45°)$.

In Fig. 6 the results of calculations of $f^{\mathrm{mol}}_{\mathrm{dom}}$, based on Eq. (A7) for a set of angles, are presented. $f^{\mathrm{gr}}_{\mathrm{dom}}$ is assumed to have the form (4).

REFERENCES

[1] W. Maier, A. Saupe, *Z. Naturforsch.* **14a**, 882 (1959).
[2] W. Maier, A. Saupe, *Z. Naturforsch.* **15a**, 287 (1960).
[3] K. Z. Ogorodnik, *Fiz. Tver. Tela* **17**, 2781 (1975); Proc. X-th All-union Conf. Phys. Liquids, Samarkand 1975, p. 185; VI-th Intern. Liq. Cryst. Conf., Kent 1976, abstr. C2-2.
[4] W. R. Krigbaum, P. C. Barber, *Acta Cryst.* **B27**, 2884 (1971); W. R. Krigbaum, T. Taga, *Mol. Cryst. Liq. Cryst.* **28**, 85 (1974); J. S. Prasad, VI-th Intern. Liq. Cryst. Conf., Kent 1976, abstr. M-2.
[5] V. I. Smirnov, *Kurs visshei matematiki*, v. 3, part 2, Moscow 1974.
[6] V. K. Dolganov, *Fiz. Tver. Tela* **18**, 1786 (1976).
[7] E. D. Cehelnik, K. D. Mielenz, R. B. Cundall, *J. Res. Natl. Bur. Stand.* **80A**, 15 (1976).
[8] E. B. Priestley, P. S. Pershan, *Mol. Cryst. Liq. Cryst.* **23**, 369 (1973).
[9] G. R. Luckhurst, R. Poupko, *Chem. Phys. Lett.* **29**, 191 (1974).
[10] S. Jen, *Raman Scattering from Liquid Crystals: A Study of Orientational Order*, Ph. D. Thesis, Harvard University, 1975.
[11] S. Jen, N. A. Clark, P. S. Pershan, E. B. Priestley, *Phys. Rev. Lett.* **31**, 1552 (1973).

[12] J.-P. Heger, *J. Phys. Lett.* **36**, 209 (1975).
[13] K. Miyano, *Phys. Lett.* **63A**, 37 (1977).
[14] V. K. Dolganov, B. M. Bolotin, *Mol. Cryst. Liq. Cryst.* **47**, 179 (1978).
[15] I. N. Dozov, I. I. Penchev, *Acta Phys. Pol.* **A54**, 649 (1978).
[16] G. R. Luckhurst, R. N. Yeates, *J. Chem. Soc. Faraday Trans. II* **72**, 996 (1976).
[17] G. R. Luckhurst, R. N. Yeates, *Mol. Cryst. Liq. Cryst.* L**34**, 57 (1976).
[18] P. S. Pershan, *The Theory of Light Scattering in Solids*, Moscow 1976, p. 61.
[19] P. J. Wojtowicz, *RCA Rev.* **35**, 118 (1974).
[20] E. B. Priestley, *RCA Rev.* **35**, 144 (1974).
[21] Denise Sy, M. Ptak, *Mol. Cryst. Liq. Cryst.* **39**, 53 (1977).
[22] K. Z. Ogorodnik, *Mol. Cryst. Liq. Cryst.* **42**, 53 (1977); *Acta Phys. Pol.* **A55**, 935 (1979).