Mesogens Orientation on Spherical Interfaces

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Abstract. The method of determination of the order parameter in surface layers oriented at spherical and cylindrical interfaces from azimuthal and radial distributions of interference bands intensity observed in polarized light is proposed. Values of the order parameter for transition state of the system ‘isotropic solution – crystal’ (benzene – para-azoxyanisole) are found.

1. Introduction
The investigation of the behavior of mesogens at the interface is very relevant since some important characteristics of liquid crystals, in particular, the anchoring energy, the order parameter, and others, are largely determined by the orientation of the mesogen molecules at the phase interface [1–4].

In previous works [5–7] we found that mesogens in solutions are oriented on spherical and cylindrical surfaces during the transition ‘isotropic solution-liquid crystal’, which allowed us to estimate the value of the order parameter from the observed interference pattern. In this connection, it is of great interest to consider how the orientational order in the surface layers of mesogen solutions changes during the isotropic solution-crystal transition.

We note that a significant change in the order parameter during the transition from an isotropic state to a liquid crystal was observed in melts of low-molecular mesogens [8, 9] and liquid-crystalline polymers [10]. The orientation of the mesogen molecules at the interface and in porous systems was considered in [11–17].

In the present work, a solution of para-azoxy-anisole in benzene at the boundary with copper wire, steel and polymer beads has been investigated with polarization microscopy.

2. Experiment and discussion
In Fig. 1 photomicrographs of the solution with a copper wire of the diameter d = 0.6 mm placed in it, are shown.
As can be seen from the figure, the crystallization of \textit{para}-azoxyanisole is observed during the evaporation of the solvent, as evidenced by the appearance of alternating dark and light strips parallel to the wire (Fig. 1). It is noted that the formation of strips, that is the crystallization of the mesogen, starts from the peripheral part of the sample at a distance several times the radius of the wire, and the crystallization front is parallel to the axis of the symmetry of the wire. The observed regularity may indicate the existence of connection between the nature of the interference pattern and the order parameter of the mesogen under study.

In Fig. 2 photomicrographs of the solution of \textit{para}-azoxyanisole in benzene, with a polymer bead (800 μm in diameter) placed in it, are presented. The photomicrographs were taken during the evaporation of the solvent. In this case, the process is also accompanied by the crystallization of \textit{para}-azoxyanisole, as evidenced by the appearance of interference fringes. Crystallization starts from the peripheral part of the sample where it is less thick. Over the time, the crystallization fronts, which in this case have a form of concentric rings, are contracted to the surface of the ball.

It is important to note that the interference fringes repeat the shape of the surface of the bead located in the center of the solution droplet (Fig. 3), not the external boundary of the sample. This
means that the solution transmits the shape of the interface with the solid phase to the crystallization region. Moreover, distance from the surface of the ball to this region exceeds the radius of the ball by an order of magnitude. It is known that an isotropic solution cannot transfer the interaction over a distance exceeding the dimensions of the molecules by 5-6 orders of magnitude. Thus, the data obtained indicate that the solution between the surface of the ball and the nuclei of crystallization is structured.

It should be noted that the observed phenomenon is slightly similar to the Leisegang rings which he detected in the course of chemical reactions in 1896 as well as to other such phenomena in dissipative structures (e.g. oscillatory chemical reactions in active media by Belousov–Zhabotinsky and other autowave phenomena). However, in those cases the structures growth was observed from the center to the periphery of perturbation. In our case the growth goes from the periphery to the center. It may be suggested that generated two-dimensional spiral autowaves transfer orientational structure information to the periphery and then cause the growth of “antispirals” from the periphery to the center.

Figure 3. A droplet of the solution of $p$-azoxyanisole in benzene with a metal ball (a) and without it (b) ($l_0 = 1.0$ mm).

The results of a similar experiment with a solution of sugar in water are shown in Fig. 4. The obtained images (polarizers crossed) indicate the absence of characteristic crystallization fronts.
3. Theory and analysis
To establish the relationship between the intensity of the observed pattern and the order parameter, the phase difference that occurs when a plane-polarized light passes through a spherical oriented mesogen layer was calculated [5]:

\[ \delta = \frac{8\pi^2N}{A_\pi} \left( \frac{n^2 + 2}{3} \right)^2 (\alpha_1 - \alpha_2) \times \]
\[ \times S \cdot \cos 2\chi \cdot r \cdot \arccos \frac{r}{R}, \]

(1)

where \( n \) – the average refractive index of the sample, \( N \) – the number of mesogen molecules per unit volume, \( \alpha_1 - \alpha_2 \) – the polarizability difference of mesogen molecules, \( R \) – the outer radius of the oriented layer, \( r \) – the radius of the light ring, \( \lambda \) – the wavelength of light, \( S \) – the order parameter, \( \chi \) – the azimuth angle. Formula (1) makes it possible to estimate the value of \( S \) from both the radial and the azimuthal distributions of the light intensity.

As can be seen from Fig. 2, the bright bands near the inner boundary of the oriented layer are located sufficiently close to each other, therefore, one can determine the order parameter \( S \) from the radial and azimuthal change in the phase difference according to the relations:

\[ \Delta \delta_r = \frac{d \delta}{dr} \Delta r = 2\pi, \]

(2)

\[ \Delta \delta_\chi = \frac{d \delta}{d\chi} \Delta \chi = 2\pi, \]

(3)

where \( \Delta r \) – the distance between two adjacent light rings, \( \Delta \chi \) – the angular distance between two neighboring minima located on one ring.

By relation (2) the values of the order parameter were obtained, which turned out equal to \( \langle \Delta S \rangle = 0.02. \)
In Fig. 5 the radial normalized intensity distribution, calculated from relation (4) is shown.

\[
\frac{i}{i_0} = \sin^2 \left( \frac{\delta}{2} \right),
\]  

(4)

where the phase difference \( \delta \) is determined from equation (1).

The following numerical values of the parameters were used for the calculation: \( n = 1.8; \) \( N = 2.5 \times 10^{21} \text{ cm}^{-1}; \) \( \alpha_1 - \alpha_2 = 2 \times 10^{-23} \text{ cm}^3; \) \( S = 0.018; \) \( R = 500 \mu\text{m} \) (a), \( 1000 \mu\text{m} \) (b), \( 2300 \mu\text{m} \) (c); \( \lambda = 0.55 \mu\text{m}. \)

The analysis of the obtained graphs allows us to conclude that the nature of the interference pattern (the number of maxima) varies drastically with the outer radius of the oriented layer.

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Fig. 2 allows us to determine the order parameter not only from the radial intensity distribution [5, 7], but also from the azimuthal one. Indeed, the angular distance between the interference maxima (minima) can be determined from the relation obtained from the condition:

\[
\Delta \delta = \delta_{m+1} - \delta_m = k\pi(m + 1) - k\pi m = k\pi,
\]  

(5)

where \( k \) – the number of the maximum, counting from the plane of polarization.

The order parameter can be determined by finding the differential of \( \delta \) in accordance with (1):

\[
\Delta \delta = \frac{16 \pi^2 N}{\lambda n} \left( \frac{n^2 + 2}{3} \right)^2 (\alpha_1 - \alpha_2) \times
\times S \cdot r \cdot \arccos \frac{r}{R} \sin 2 \chi \Delta \chi = k\pi,
\]  

(6)

where \( \Delta \chi \) – the azimuth difference between the two nearest interference maxima located on the same ring of the radius \( r. \) This value is determined from the micrograph (Fig. 2). The value of the order parameter obtained this way is equal to \( S = 0.013. \)

In Fig. 6 the modeled spatial distribution of the relative intensity of the interference fringes for different values of \( R / \lambda \) is shown:
Figure 6. Models of the spatial distribution of the relative intensity of interference bands.

These models reflect the dependence of the interference pattern on the radius of the oriented layer. A similar picture (an increase in the number of interference maxima) along the radius and the azimuth is observed in dynamics of the formation of the oriented layer (Fig. 2), as well.

4. Conclusions
- The method of determining the order parameter in surface layers oriented towards spherical surfaces from the azimuthal and radial intensity distributions of interference bands has been developed.
- Values of the order parameter for the studied systems have been defined.
- It has been shown that values of the order parameter defined from the radial and azimuthal intensity distributions vary slightly.
- Models of the spatial intensity distribution have been constructed.

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